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REACTIONS BETWEEN ACID AND BASIC AMIDES IN LIQUID AMMONIA.

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The close analogy existing between liquid ammonia and water as electrolytic solvents has been shown in some recent papers by Franklin and Kraus.[1] Among other points of analogy these authors call attention to the fact that acid and basic amides bear a relation to liquid ammonia which in many respects is very similar to that borne by ordinary acids and bases to water. Conductivity measurements, for example, have shown that ammonia solutions of acid and basic amides are conductors of electricity, a fact due presumably, since ammonia itself has a conductivity of the same order as that of water,[2] to the dissociation of the basic amides into metal cation and amide anion,

$$MeNH_2 \rightleftarrows Me^{\cdot} + NH'_2,$$

and a similar dissociation of the acid amide into acid anion and hydrogen ion, or, more probably, hydrogen associated with ammonia as ion, as indicated herewith,

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[1] This JOURNAL, **20**, 820 (1898); **20**, 836 (1898); **21**, 1 (1899); **21**, 9 (1899); **23**, 277 (1900).

[2] Franklin and Kraus: *Ibid.*, **23**, 285 (1900); Frenzel: Ztschr. Elektrochemie, **6**, 479 (1900).

$$AcNH_2 \rightleftarrows AcNH' + H^{\cdot} \text{ or } H(NH_3)^{\cdot}_n.$$

Further, since the acid amides contain two amide hydrogen atoms, it is probable that equilibrium also exists between the anion AcNH' and its dissociation-products as indicated in the equation

$$AcNH' \rightleftarrows Ac'' + H^{\cdot} \text{ or } H(NH_3)^{\cdot}_n.$$

This view of the acid and basic characters of the amides in question would seem to be further substantiated by their power, when in ammonia solution, to bring about many of the identical color changes that are characteristic of the well-known indicators used in acidimetry and alkalimetry.[1]

These considerations, taken together with the facts developed in the papers above mentioned bearing upon the close similarity existing between water and ammonia as solvents, make it highly probable that in ammonia solutions reactions should occur between acid and basic amides with all the facility that marks the interaction of ordinary acids and bases in water. At the risk of being unnecessarily explicit, the following parallel reactions are given for the potassium hydroxide-acetic-acid-water system and the analogous potassium-amide-acetamide-ammonia system :

$$K^{\cdot} + OH' + CH_3COO' + H^{\cdot} = CH_3COO' + K^{\cdot} + H_2O\,;$$
$$K' + NH'_2 + CH_3CONH' + H^{\cdot} = CH_3CONH' + K^{\cdot} + NH_3\,;$$

and since there is a second amide hydrogen atom in the acid amide, another reaction is theoretically possible in the ammonia system,

$$K^{\cdot} + NH'_2 + CH_3CON'' + H^{\cdot} + K^{\cdot} = CH_3CON'' + 2K^{\cdot} + NH_3.$$

These reactions, written in the ordinary molecular formulæ, are :

$$KOH + CH_3COOH = CH_3COOK + H_2O\,;$$
$$KNH_2 + CH_3CONH_2 = CH_3CONHK + NH_3\,;$$
$$2KNH_2 + CH_3CONH_2 = CH_3CONK_2 + 2NH_3.$$

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[1] *Loc. cit.*

The substances formed in this way should, in all probability, be salt-like bodies appearing as precipitates in case they are insoluble, or in case they are soluble, allowing themselves to be crystallized from their solutions.

As a matter of fact, many compounds of the kind in question have been prepared and are described in the literature,[1] but by one investigator only have any of them been made by the interaction of acid and basic amides. Titherly[2] has obtained the sodium derivatives of formamide, acetamide, propionamide, and benzamide as amorphous precipitates by the continued action of hot benzene solutions of the acid amides upon sodium amide. Some qualitative experiments by Franklin and Kraus[3] show that compounds of this class are formed with marked facility when the acid and basic amides are brought together in ammonia solution.

Theoretically, then, it would seem that the possibilities for the formation of new compound in the ammonia system would be limited only by the number of available acid and basic amides. There is a corresponding acid amide for nearly every one of the known oxygen acids, and when to this class of compounds are added the nitrides of the non-metallic elements and the whole list of ammonium salts, which have been shown to be analogous in some respects, when in ammonia solution, to the oxygen acids in water, the number of substances that might be expected to act as acids is very great. On the other hand, the number of substances capable of acting as bases is somewhat limited. Many metallic nitrides have been prepared, but the number of known basic amides is small. Of the metallic amides analogous to the hydroxides only those of sodium,[4] potassium,[4] lithium,[5] calcium,[6] and zinc[7] have been described, though the fact that solutions of potassium amide give precipitates in ammonia solution[1] with the salts of many of the heavier metals makes it probable that by this method a considerable number of new amides may be prepared.

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[1] **Dessaignes**: Ann. Chem. (Liebig), **82**, 231 (1852); **Frankland**: Jsb., 1857, p. 419; **Strecker**: Ann. Chem. (Liebig), **103**, 324 (1857); **Landsberg**: *Ibid.*, **215**, 172 (1882); **Gal**: Bull. soc. chim., **39**, 647 (1883); **Curtius**: Ber. d. chem. Ges., **23**, 3037 (1891); **Blacher**: *Ibid.*, **28**, 432 and 2352 (1895); **Titherly**: J. Chem. Soc. (London), **71**, 461 (1897).

[2] *Loc. cit.*

[3] *Loc. cit.*

[4] **Gay Lussac and Thenard**: Watts' Dict., Vol. IV., pp. 299 and 475 (1894); **Beilstein and Geuther**: Ann. Chem. (Liebig), **108**, 88 (1858); **Baumer and Landolt**: Ann. Chem. (Liebig), **111**, 1 (1859); **Joannis**: Compt. rend., **112**, 392 (1891).

[5] **Titherly**: J. Chem. Soc. (London), **65**, 504 (1894).

[6] **Moissan**: Bull. soc. chim., [3], **21**, 909 (1899).

[7] **Frankland**: *Loc. cit.*

Hence it appears that the theoretical possibilities for salt formation in the ammonia system might be expected to approach in extent that of the water system. It has therefore seemed worth while to study the products of the interaction of one or two typical basic amides with several of the available acid amides, to confirm, if possible, the theoretical considerations just advanced.

Method of Preparation.

An idea of the method used in making most of the substances described in this paper can be obtained from the following account of the preparation of a potassium compound. A weighed quantity of metallic potassium is introduced into the preparation tube (Fig. I.), which has previously been filled to about the point *a* with liquid ammonia. The metal dissolves at once, forming a characteristic blue solution.[2] Upon allowing the preparation to stand, the blue color gradually disappears with the evolution of hydrogen gas. This decolorizing process, which marks the gradual change of potassium-ammonium into potassium amide, requires several hours. It is usually desirable, therefore, to seal the tube at β, withdraw it from the bath of liquid ammonia, in which it is necessary to keep it while open, and allow it to stand at laboratory temperature until needed. In case the quantity of metal introduced is large, it has been found advisable to open the tube occasionally to permit the accumulated hydrogen to

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[1] For example, when a solution of potassium amide is added to a solution of nickel nitrate a chocolate-colored precipitate is formed. Lead nitrate or lead iodide gives a yellow precipitate, calcium nitrate and zinc nitrate give white precipitates, while with copper nitrate and magnesium nitrates no precipitates are produced. When potassium amide solution is added to a solution of silver nitrate or iodide a white precipitate is formed which, when dry, is exceedingly explosive. A number of attempts to determine the atomic ratio between the silver and nitrogen in this compound indicate the probable formation of silver amide. The results of the study of these reactions will be given in a future paper.

[2] This blue liquid behaves in most respects like a simple solution of metallic potassium in liquid ammonia. According to Joannis (Compt. rend., **115**, 820 (1898)) the solution contains the compound $KNH_2—NH_3K$, which he calls potassammonium.

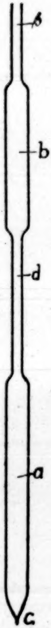

Fig. I.

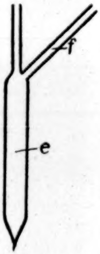

Fig. II.

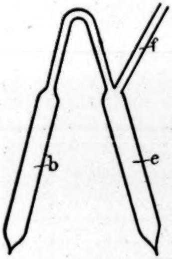

Fig. III.

escape. The resulting solution of potassium amide is a clear, mobile liquid, generally of a light-yellow color. Usually there is mixed with it more or less potassium hydroxide in the form of an amorphous, insoluble mass, the reaction-product, doubtless, of moisture that in various ways might enter the tube during the introduction of the materials used. By careful decantation of the liquid into the other end of the tube, however, the precipitate may be retained in the arm *a*, with which it is subsequently removed, the tube being cut at *d* for this purpose after taking the precautions—always necessary in opening and closing tubes containing liquid ammonia

—to cool the contents in a bath of liquid ammonia and to insure the absence of all internal pressure by opening the capillary at *c*. In place of the part removed is sealed the receptacle shown in Fig. II., after which the apparatus is bent into the form shown in Fig. III., the two arms being left divergent to facilitate the transference of liquid from one arm to the other. With the arm *b* still immersed in liquid ammonia, a weighed quantity of the acid amide is introduced into the arm *e* through the tubulure *f*. In case the apparatus contains an insufficient quantity of liquid for the operations to follow, *e* is immersed in a cooling-bath and the requisite quantity of ammonia is introduced through *f* from a pipette. The tubulure is then closed before the blowpipe, care being taken to avoid contamination of the contents of the apparatus with moisture from the flame. In case no ammonia has been placed directly upon the acid amide by introduction through *f* as just described, the arm *e* of the sealed apparatus is placed in a cooling-bath—most frequently in these experiments liquid ammonia itself—whereupon the solvent rapidly distils over from *b* and immediately dissolves the amide. The tube is then permitted to warm up to the temperature of the laboratory. If now either solution be poured into the other the results of the reaction can be observed. In case a precipitate is produced the mother-liquor is poured therefrom into the empty arm of the tube and pure ammonia is distilled from this mother-liquor back upon the solid substance. This ammonia, after agitation with the precipitate, is again poured back into the other arm of the apparatus. This operation is repeated as often as may be considered desirable. The arm of the tube containing the washed substance is at last sealed off to a long capillary point through which the vapor of the solvent may escape slowly, and so prevent the violent boiling and bumping—entailing always the risk of mechanical loss of material—that usually accompanies the evaporation of liquid ammonia from open narrow tubes. As soon as the last traces of liquid disappear the tube is sealed and preserved until its contents are needed for further examination.

The object in view in undertaking this investigation was to demonstrate the existence of certain compounds rather than to make any detailed study of their properties. The work, therefore, has been confined almost entirely to the preparation and analysis of the substances to be described, although incidentally some properties were observed. In general, it may be said that the compounds are easily soluble in water, in which they suffer more or less complete hydrolysis. The amides used, both basic and acid, are easily soluble in liquid ammonia, though the products of their interaction present the greatest diversity of solubility in that medium. Some of the potassium compounds, for example, are apparently insoluble, others so very soluble that a separation of the solid substances from the mother-liquors is impossible, while between these two extremes are compounds the solubility of which permits their ready recrystallization.

Methods of Analysis.

The difficulties encountered in the analytical part of the work were not inconsiderable. The intensely hygroscopic character of the compounds, indeed, has rendered the questions of proper desiccation and accurate weighing among the most serious problems in the research. Many of the compounds stand heating, without apparent decomposition, to 100° in the double-tube arrangement shown in Fig. IV., in which

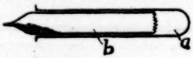

Fig. IV.

b is the opened preparation-tube and *a* a snugly fitting test-tube. This treatment generally drives off the adherent ammonia completely, while the diffusion of water vapor into the apparatus from the atmosphere is negligible. In some cases, however, especially in the presence of traces of moisture, incipient decomposition is produced which is itself productive of ammonia. The dividing line between these two kinds of ammonia is sometimes exceedingly hard to locate, a fact that has done much to render certain of the analytical results less concordant than is desirable, though it is thought that in none of the cases given below are the discrepancies great enough to bring the identity of the compounds into question.

Nitrogen was determined partly by the absolute method of Dumas and partly by the Kjeldahl method. In using the latter the hydrolysis of the compound was insured by treating it with hot sulphuric acid, after which the solution was made alkaline, and the ammonia distilled by the aid of a current of steam into standard acid.

Potassium was determined by igniting the salt and subsequently converting the residue into the sulphate according to the directions of Fresenius.

Magnesium was weighed as magnesium pyrophosphate. The salt was hydrolyzed by treatment with hydrochloric acid after which the usual procedure, as described by Fresenius, was followed.

Sulphur was converted into the sulphate ion and weighed as barium sulphate, according to the method of Carius.

Potassium Salts.

The greater number of compounds described in this paper have been made by the action of potassium amide on the respective acid amides. The reasons which have led us to study especially the potassium salts are the much greater solubility of potassium amide over that of the other known metallic amides and the greater ease with which this basic amide is formed by the interaction of the metal and liquid ammonia. A quantity of potassium-ammonium contained in one of the above-described preparation-tubes is usually completely decomposed after a few hours at laboratory temperature, while the decomposition of sodium-ammonium or lithium-ammonium is complete only after the lapse of many days. In the case of several tubes containing sodammonium, the transformation into sodium amide was not finished even after standing for six months. Potassium amide is very soluble in liquid ammonia. It separates from very concentrated solutions as a colorless, well-crystallized, highly hygroscopic mass. Beautiful crystals are formed when the solution is carefully evaporated. Joannis[1] has shown that the action of ammonia on the ammonia solution of metallic potassium is represented by the equation

$$K + NH_3 = KNH_2 + H,$$

and while it is probably unnecessary for the identification of the compound we have, nevertheless, made determinations of the potassium in two specimens of the substance, as follows:

I. 0.1250 gram substance gave 0.1654 gram KCl.
II. 0.1198 gram substance gave 0.1626 gram KCl.

	Calculated for KNH_2.	Found. I.	II.
K	70.90	69.44	71.10

Monopotassium Acetamide, $CH_3CONHK.nNH_3$. — When equimolecular quantities of potassium amide and acetamide are brought together in the apparatus described above and the solution is cooled in a bath of liquid ammonia, colorless crystals of monopotassium acetamide separate from the concentrated solution. Since the substance is very soluble in ammonia it was not possible to wash the crop of crystals. The product was therefore simply drained of mother-liquor, dried at laboratory temperature, and submitted to analysis with the following results:

I. 0.1628 gram salt gave 0.1380 gram K_2SO_4.
II. 0.3500 gram salt gave 0.0499 gram N.
III. 0.1357 gram salt gave 0.1184 gram K_2SO_4.

	Calculated for CH_3CONHK.	Found. I.	II.	III.
K	40.21	38.09	....	39.21
N	14.44	....	14.26	....

The same substance is also formed by the action of metallic potassium on a solution of acetamide. The action is very vigorous and is accompanied by the evolution of hydrogen gas. Monopotassium acetamide contains ammonia of crystallization, which escapes rapidly at laboratory temperature and atmospheric pressure. During this drying the crystals lose their transparency and take on the opaque appearance exhibited by bodies which have effloresced.

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[1] *Loc. cit.*

Dipotassium Acetamide, CH_3CONK_2, is probably formed when solutions containing 2 molecules of potassium amide and 1 molecule of acetamide are brought together. The product, however, is so extremely soluble that it cannot be drained of mother-liquor for analysis. At the temperature of the ammonia-bath it crystallizes from very concentrated solutions to a nearly solid mass, which melts as soon as the temperature is allowed to rise.

Monopotassium Phenylacetamide, $C_6H_5CH_2CONHK.nNH_3$.—When phenylacetamide and potassium amide are brought together in molecular proportions and the solution is cooled to —33°, a crop of beautiful, needle-like crystals fills the tube. At higher temperatures these crystals dissolve very easily. Upon drying they lose their luster, and must consequently contain ammonia of crystallization.

0.1067 gram salt gave 0.0540 gram K_2SO_4.
0.1491 gram salt gave 0.0755 gram N.

	Calculated for $C_6H_5CH_2CONHK$.	Found.
K	22.60	22.72
N	8.11	5.06

Monopotassium Benzamide, C_6H_5CONHK.—When equimolecular quantities of benzamide and potassium amide are brought together in ammonia solution a bulky, crystalline precipitate of the monopotassium salt is formed. The compound which apparently does not contain ammonia of crystallization, is somewhat soluble in ammonia and in excess of the acid amide. It is also soluble in excess of the basic amide.

I. 0.0765 gram salt gave 0.0418 gram K_2SO_4.
0.1592 gram salt gave 0.01384 gram N.
II. 0.0576 gram salt gave 0.0309 gram K_2SO_4.
0.0865 gram salt gave 0.00482 gram N.

	Calculated for C_6H_5CONHK.	Found.	
		I.	II.
K	24.60	24.54	24.10
N	8.81	8.70	5.58

Dipotassium Benzamide, $C_6H_5CONK_2$, is formed as a bulky, crystalline precipitate when two molecular weights of potassium amide are mixed with one molecular weight of benzamide in ammonia solution. The salt is somewhat soluble.

	Calculated for $C_6H_5CONK_2$.	Found.
K	39.66	....
N	7.11	7.12

Monopotassium Benzenesulphonamide, $C_6H_5SO_2NHK$.—Upon adding an equivalent quantity of the acid amide to potassium amide a solid substance forms at the junction of the two solutions and completely separates them. Upon agitation, however, everything passes into solution, and after a short time colorless, well-formed crystals separate, especially from the cold solution. The salt is fairly soluble in ammonia, very easily soluble in excess of acid amide, but insoluble in excess of the basic amide. The crystals lost neither form nor luster when heated to the temperature of boiling water. They must consequently be free from ammonia of crystallization.

I. 0.3623 gram salt gave 0.1598 gram K_2SO_4.
II. 0.1942 gram salt gave 0.0824 gram K_2SO_4.
III. 0.0850 gram salt gave 0.0380 gram K_2SO_4.
0.1939 gram salt gave 0.0131 gram N.

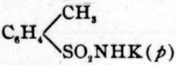
	Calculated for $C_6H_5SO_2NHK$.	Found.		
		I.	II.	III.
K	20.04	19.79	19.05	20.10
N	7.19	....	....	6.78

Dipotassium Benzenesulphonamide, $C_6H_5SO_2NK_2$.—Benzenesulphonamide, when added to an excess of potassium amide, produces a very bulky, amorphous precipitate which refuses to settle and which consequently cannot be well washed. In the case of the preparation numbered II below, the liquid was evaporated completely from the precipitate in the hope of getting the substance into a better condition for washing. The result was that a sticky, amorphous mass remained clinging to the walls of the tube in such a condition as to render thorough washing impracticable. The low results obtained may very well be due to the presence of the monopotassium salt, which was protected during the process of washing by the insoluble dipotassium salt.

I. 0.2599 gram salt gave 0.1852 gram K_2SO_4.
II. 0.1702 gram salt gave 0.1132 gram K_2SO_4.

	Calculated for $C_6H_5SO_2NK_2$.	Found. I.	II.
K	33.53	32.00	29.80

Monopotassium Paratoluenesulphonamide,



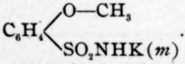
$C_6H_4<\begin{matrix}CH_3\\SO_2NHK(p)\end{matrix}$.—When potassium amide and *p*-toluenesulphonamide are mixed an amorphous precipitate is formed which is insoluble in excess of either acid or basic amide. The salt for which the analysis is given below was made by adding potassium amide solution to a solution of the acid amide until a sufficient quantity of the monopotassium compound for analysis was obtained.

0.1058 gram salt gave 0.0392 gram K_2SO_4.

0.1505 gram salt gave 0.0172 gram N.

	Calculated for $C_7H_7SO_2NHK$.	Found.
K	16.31	16.64
N	6.71	11.42

Monopotassium Metamethoxybenzenesulphonamide,



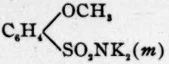
$C_6H_4<\begin{matrix}O{-}CH_3\\SO_2NHK(m)\end{matrix}$.—A crop of small, well-formed crystals without ammonia of crystallization is formed when equimolecular quantities of potassium amide and metamethoxybenzenesulphonamide are brought together in ammonia solution. The salt is distinctly soluble.

0.1149 gram salt gave 0.0436 gram K_2SO_4.

0.1782 gram salt gave 0.1849 gram $BaSO_4$.

	Calculated for $C_7H_7OSO_2NHK$.	Found.
K	17.36	17.03
S	14.21	14.24

Dipotassium Metamethoxybenzenesulphonamide,

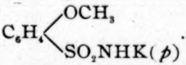


$C_6H_4<\begin{matrix}OCH_3\\SO_2NK_2(m)\end{matrix}$.—An insoluble, apparently amorphous precipitate of the dipotassium salt of metamethoxybenzenesulphonamide is formed when 1 molecule of the acid amide is added to 2 molecules of potassium amide. The precipitate settles well and is easily washed for analysis. The salt contains no ammonia of crystallization.

0.1256 gram salt gave 0.0822 gram K_2SO_4.
0.0595 gram salt gave 0.0518 gram $BaSO_4$.

	Calculated for $C_7H_7OSO_2NK_2$.	Found.
K	29.73	29.39
S	12.13	11.96

Monopotassium Paramethoxybenzenesulphonamide,

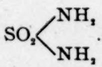


$C_6H_4{<}\begin{matrix}OCH_3\\SO_2NHK(p)\end{matrix}$.—When potassium amide is added to a solution of paramethoxybenzenesulphonamide a precipitate is formed which is soluble in excess of the acid amide. The salt does not settle well, is crystalline and somewhat soluble in ammonia. It does not contain ammonia of crystallization.

I. 0.0517 gram salt gave 0.0042 gram N.
II. 0.1740 gram salt gave 0.00936 gram N.
III. 0.0665 gram salt gave 0.0053 gram N.
0.0747 gram salt gave 0.0258 gram K_2SO_4.

	Calculated for $C_7H_7OSO_2NHK$.	Found. I.	II.	III.
K	17.36	....	....	16.35
N	6.23	8.11	5.38	7.98

Dipotassium Paramethoxybenzenesulphonamide, $C_6H_4OCH_3SO_2NK_2$, is presumably formed as a very bulky, insoluble precipitate when 1 molecule of paramethoxybenzenesulphonamide is added to 2 molecules of potassium amide. The precipitate fills the whole tube and refuses to settle. It was therefore impracticable to wash the precipitate for analysis.



Sulphamide, $SO_2{<}\begin{matrix}NH_2\\NH_2\end{matrix}$.—Sulphamide[1] was prepared according to the directions given by Traube.[2] It is very soluble in liquid ammonia, even deliquescing in the vapor given off by the cold liquid. Indeed, it absorbs ammonia so rapidly that the liquid in the second arm of the closed preparation-tube boiled vigorously even when covered with ice. The resulting solution is viscid and colorless, but when diluted forms a clear, mobile liquid. The solution discharges the red color produced in an ammonia solution of phenolphthalein by potassium amide, and is a good conductor of electricity.

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[1] A sample of sulphamide made by Schuchardt was found to contain over 90 per cent of ammonium sulphate.

[2] Ber. d. chem. Ges., **26**, 607 (1893).

Since the molecule of sulphamide contains four amide hydrogen atoms it would seem that it perhaps ought to be possible to prepare four potassium sulphamide derivatives. Investigation, however, has proved the existence of the mono- and dipotassium salts only.

Monopotassium Sulphamide, $SO_2N_2H_3K$.—When potassium amide is added to a solution of an equivalent quantity of sulphamide an amorphous, white precipitate is formed, which is not appreciably soluble in excess of either acid or basic amide. A determination of potassium in which losses were known to occur during the analysis, resulted as follows :

0.0762 gram salt gave 0.0451 gram K_2SO_4.

	Calculated for $SO_2N_2H_3K$.	Found.
K	29.10	26.70

Further analyses of this salt have not yet been made for the reason that the small quantity of the acid amide prepared was too soon exhausted.

Dipotassium Sulphamide, $SO_2N_2H_2K_2$.—A bulky, amorphous precipitate of the dipotassium salt of sulphamide is formed when 1 molecule of the acid amide is added to 2 molecules of potassium amide. Because of the difficulty encountered in washing the bulky precipitate, the purity of the sample submitted to analysis was not assured. The solvent was completely evaporated from the precipitate in an attempt to get it into better condition for washing. This was not successful, however, for the precipitate then remained plastered to the walls of the tube in such a form as to prevent efficient action of the washing liquid.

0.2069 gram salt gave 0.02816 gram N and 0.2928 gram $BaSO_4$.

	Calculated for $SO_2N_2H_2K_2$.	Found.
N	16.29	13.78
S	18.59	19.43

Losses of nitrogen were known to have occurred during the progress of the analysis.

In another experiment, in which the quantity of potassium amide used was in considerable excess of the amount necessary for the formation of the dipotassium salt, a determination of the potassium in the product resulted as follows:

0.1385 gram salt gave 0.1364 gram K_2SO_4.

	Calculated for $SO_2N_2H_2K_2$.	Found.
K	45.41	44.26

An attempt was made to obtain a salt in which more than 2 atoms of potassium are present in the molecule. To this end 1 molecule of sulphamide was added gradually to somewhat more than 4 molecules of potassium amide, and the mixture with the excess of basic amide was, after being thoroughly shaken, allowed to stand for five days at laboratory temperature. A bulky, amorphous, insoluble precipitate, similar in appearance to those obtained above, was the result. The product could not be thoroughly washed.

0.0570 gram salt gave 0.0630 gram K_2SO_4.

	Calculated for $SO_2N_2H_2K_2$.	Found.
K	45.41	49.62

Hence, it seems that compounds containing more than 2 atoms of the metal cannot be formed under these circumstances. The high results obtained for the potassium content of the preparation may be due to the incomplete removal of the admixed potassium amide, or, it may be, that some tri- or even tetrapotassium salt is formed in the presence of a large excess of the basic amide which is then not entirely decomposed, hydrolyzed, and removed during the subsequent washing.

Urea, CON_2H_4.—The considerations concerning the possible existence of four potassium derivatives of sulphamide apply to the case of urea, which, likewise, contains four amide hydrogen atoms. As in the previous case, however, investigation has shown that the tri- and tetrametallic derivatives are not formed.

Monopotassium Urea, CON_2H_3K.—Upon mixing solutions containing equivalent quantities of urea and potassium amide a white precipitate immediately forms which fills the whole arm of the preparation-tube as an amorphous mass. If, however, the potassium amide be added to the urea, a drop at a time, then a tough osmotic membrane of the potassium salt forms around each drop, enclosing it and protecting it from further action of the acid amide. These globules are easily broken up by agitation, however, and the precipitate goes into solution in the excess of urea. At a certain stage in the process of adding the basic amide the conditions become such that a cloudiness is produced. Cooling the solution at this stage causes the disappearance of the cloudiness, which appears again on warming the tube. At somewhat greater concentration, and at the temperature of the laboratory, two liquid layers appear. If the tube is again cooled the contents of the tube again become homogeneous. On warming the tube the cloudiness again appears, followed by the formation of the two liquid layers. In more concentrated solutions the separation into two liquid layers cannot be accomplished. After the addition of the full equivalent of potassium amide, the monopotassium salt slowly separates out on the walls and bottom of the tube in the form of minute, colorless crystals. Unless the addition of the potassium amide is carefully carried out the precipitate is formed as an amorphous mass which cannot be well washed, a fact which probably accounts for the divergent analytical results.

I. 0.2494 gram salt gave 0.2580 gram K_2SO_4.
II. 0.3645 gram salt gave 0.3435 gram K_2SO_4.
III. 0.2374 gram salt gave 0.2104 gram K_2SO_4.
IV. 0.3286 gram salt gave 0.0980 gram N.
V. 0.1856 gram salt gave 0.0544 gram N.
0.1210 gram salt gave 0.1017 gram K_2SO_4.
VI. 0.1316 gram salt gave 0.0364 gram N.
VII. 0.1149 gram salt gave 0.1000 gram K_2SO_4.
VIII. 0.2874 gram salt gave 0.0864 gram N.

	Calculated for CON_2H_3K.	Found.							
		I.	II.	III.	IV.	V.	VI.	VII.	VIII.
K	39.75	46.45	42.30	39.80	....	37.75	....	39.74	....
N	28.50	....	....	....	29.80	29.30	27.67	....	30.45[1]

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[1] The specimen used for making this determination was not free from ammonia.

Dipotassium Urea, $CON_2H_2K_2$.—If the order of the process described above for bringing the solutions together be reversed, that is, if the acid amide be poured into the basic amide solution, a permanent, gelatinous precipitate is produced, which the analyses show to be probably a mixture of the dipotassium salt with more or less of the monopotassium compound. An ammonia solution of urea is a very poor conductor of electricity. Urea must therefore be regarded as a very weak acid from which it follows that hydrolysis of the dipotassium salt may account for the divergent analytical results here recorded.

Analyses of products formed by the interaction of 1 molecule of urea with 2 molecules of potassium amide are as follows:

I. 0.1301 gram salt gave 0.1685 gram K_2SO_4.
II. 0.1058 gram salt gave 0.0244 gram N.
III. 0.1205 gram salt gave 0.0275 gram N.
IV. 0.1341 gram salt gave 0.0307 gram N.
V. 0.1205 gram salt gave 0.0266 gram N.
VI. 0.1288 gram salt gave 0.1370 gram K_2SO_4.
VII. 0.0713 gram salt gave 0.0770 gram K_2SO_4.
VIII. 0.2041 gram salt gave 0.0500 gram N.
IX. 0.1761 gram salt gave 0.0374 gram N.
X. 0.2522 gram salt gave 0.0545 gram N.
XI. 0.1796 gram salt gave 0.0365 gram N.

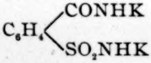
	Calculated for $CON_2H_2K_2$.	Found.					
		I.	II.	III.	IV.	V.	VI.
K	57.42	58.11	....	....	....	....	47.60
N	20.60	....	23.10	22.80	22.94	22.05	....

	Calculated for $CON_2H_2K_2$.	Found.				
		VII.	VIII.	IX.	X.	XI.
K	57.42	48.40	....	....	....	....
N	20.60	....	24.53	21.28	21.59	20.30

In two experiments in which 1 molecule of urea was added to something over 3 molecules of potassium amide, and the tubes were allowed to stand several days to complete the reaction, analysis of the gelatinous precipitate gave the following results:

I. 0.1200 gram salt gave 0.0248 gram N.
II. 0.0779 gram salt gave 0.995 gram K_2SO_4.

	Calculated for $CON_2H_2K_2$.	Found. I.	Found. II.
K	57.42	....	57.33
N	20.60	20.65	....

Potassium Saccharin.—When potassium amide is added to a solution of saccharin a gelatinous precipitate is formed which surrounds each drop of the basic amide solution as an osmotic membrane. On agitation the precipitate dissolves in excess of the acid imide. Further addition of the basic amide produced a permanent precipitate, which gave widely divergent analytical results. In five experiments the precipitate formed by the addition of 1 molecule of potassium amide to 1 molecule of saccharin gave from 22.20 to 26.67 per cent potassium. The calculated percentage of potassium in $C_6H_4SO_2CONK$ is 17.67. When 2 molecules of potassium amide were added to 1 of saccharin, two experiments gave respectively 33.08 and 30.20 per cent potassium, while three further experiments gave 11.69, 9.80, and 11.74 per cent sulphur. It seems probable that the compound  $C_6H_4\begin{cases}CONHK\\SO_2NHK\end{cases}$ is formed, but the exhaustion of the supply of saccharin prevented further investigation along this line.

Other Potassium Derivatives.

Attempts were made to prepare potassium salts of a considerable number of other acid amides, but while action evidently took place in each instance, for various reasons no products were isolated.

Formamide.—When a solution of 1 molecule of potassium amide is added to 1 molecule of formamide, and the solution is cooled in a bath of liquid ammonia, a crop of beautiful needle-like crystals separate from the solution. Decomposition accompanied by the evolution of hydrogen immediately sets in, however, and in a short time the crystals disappear and cannot be again obtained.

Dichloracetamide.—On mixing dichloracetamide and potassium amide the solution rapidly became strongly colored. After a time a brick-red precipitate separated, but this soon disappeared and the contents of the tube became less and less promising as time passed.

Thioacetamide.—When potassium amide solution is added to a solution of thioacetamide a precipitate is formed which quickly dissolves in excess of the acid amide. The monopotassium salt, if such is formed, is so very soluble in ammonia that a product for analysis could not be isolated. With potassium amide in excess a permanent precipitate is produced, but the attempt to purify this substance for analysis was not made.

Cyanacetamide.—On adding 1 molecule of potassium amide to 1 molecule of cyanacetamide a precipitate is produced which immediately dissolves when the contents of the tube are mixed. Cooling caused no separation of crystals. On evaporating the solution a thick, viscous residue was left, which dried finally to a frothy mass which foamed up and almost filled the tube. This residue is very deliquescent in ammonia vapor. At a certain stage during the deliquescence, crystalline nuclei made their appearance and gradually spread through the mass only to disappear again as the absorption of ammonia continued. This very soluble, deliquescent substance is in all probability the monopotassium salt of cyanacetamide. Attempts were not made to prepare the dipotassium salt.

Parachlorbenzamide.—When potassium amide is added to a solution of parachlorbenzamide, a fugitive, colored precipitate is formed which dissolves instantly in excess of the acid amide to form a red solution. When the acid amide is added to the potassium amide a green solution results, with no indication of a precipitate. From the red solution formed by mixing equimolecular quantities of the acid and basic amides it is possible, in the cold and from very concentrated solutions, to obtain an exceedingly soluble mass of crystals, presumably of monopotassium parachlorbenzamide. The attempt to separate them for analysis was not made.

Succinimide gave a precipitate with potassium amide, but on standing the precipitate became so strongly colored and unpromising in appearance that the experiment was discontinued.

Thiourea.— The behavior of thiourea solutions, when brought into contact with potassium amide, is almost identical with that exhibited by ordinary urea. The precipitates are much more gelatinous, however, and much less stable than the urea compounds, suffering decomposition at the temperature used for drying the latter. Indeed, so much difficulty was encountered in this respect that no concordant analytical results have been obtained.

Allylthiourea.—The addition of 1 molecule of potassium amide to 1 molecule of the acid amide produced no permanent precipitate. When the solution is very concentrated and is kept cooled for some time the viscous residue changes into a mass of crystals, which very soon liquefy on being removed from the bath of liquid ammonia. With potassium amide in excess a much less soluble product is obtained.

Trinitraniline (*Picramide*).—The well-known acid properties of trinitrophenol and the fact that trinitraniline is a fair conductor[1] of electricity when in solution in liquid ammonia, suggests the possibility of metathetic action between the latter and potassium amide. Picramide is very easily soluble in ammonia, with which it forms a deep-red solution. On adding potassium amide to a solution of picramide an amorphous, dark-colored precipitate is formed, which quickly dissolves in excess of the acid amide. With further additions of the basic amide, a good crop of well-formed crystals are deposited. The crystals slowly disappear, however, even when the tube is kept cold. After an hour or two they have completely disappeared and cannot again be obtained. Evaporation of the solvent leaves a strongly colored, viscous mass, from which a product for analysis could not be obtained. It seems probable that metathetic action actually takes place but that the result is obscured by deep-seated changes which rapidly follow.

Metanitroparatoluidine, with potassium amide, gave a strongly colored solution from which no product for analysis could be separated.

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[1] Measurements by Franklin and Kraus.

Sodium Salts.

Metallic sodium dissolves readily in liquid ammonia, forming a blue solution to all outward appearances, identical with the potassium solution described above.

Sodium amide formed by the decomposition of sodammonium is a perfectly colorless substance which separates from the ammonia solution as well-formed, granular crystals. An analysis of a specimen thus prepared gave the following results:

0.0702 gram amide gave 0.1264 gram Na_2SO_4.
0.0366 gram amide gave 0.01286 gram N.

	Calculated for $NaNH_2$.	Found.
Na	58.95	58.38
N	35.90	35.13

Monosodium Acetamide, $CH_3CONHNa.nNH_3$.—This compound is formed when equimolecular quantities of sodium amide and acetamide are brought together in ammonia solution. It dissolves readily in ammonia, but is not so soluble as the potassium salt. Like the potassium derivative, it separates with ammonia of crystallization. Since, in the preparation of the specimen for which the analysis is given, considerable excess of acetamide was used which could not be removed by washing on account of the ready solubility of the salt, contamination with acetamide probably accounts for the results obtained.

	Calculated for $CH_3CONHNa$.	Found.
Na	28.43	21.83

Sodium acetamide is also formed by the action of a solution of acetamide on metallic sodium. The action is vigorous and is accompanied by the evolution of hydrogen. The salt separates as a crop of well-formed crystals from the concentrated solution.

Magnesium Salts.

If the condition of acid amides in solution in liquid ammonia is analogous to the condition of the oxygen acids in aqueous solution, then solutions of the former should attack at least the more electropositive metals with the evolution of hydrogen. That such action does take place very readily in the case of sodium and magnesium, and to some slight extent in the case of zinc, has already been pointed out by Franklin and Kraus.[1]

While acetamide acts readily on sodium, potassium and magnesium, experiments in which zinc, iron, aluminum, and copper were left in contact with acetamide solution for six months, show these metals to be entirely unaffected. Benzenesulphonamide acts rapidly on sodium and potassium, more slowly upon magnesium, and very slowly on zinc. The zinc is soon coated with a yellowish, insoluble crust, presumably of zinc benzenesulphonamide, which stops further action.

Of the acid amides whose action on magnesium has been tested, acetamide, benzenesulphonamide, benzoic sulphinide, benzamide, phenylacetamide, cyanacetamide, and cyanamide have been found to attack the metal while formamide, toluenesulphonamide, succinamide, and sulphamide have been found to be without appreciable action. Magnesium, as well as sodium and potassium, are also readily attacked by solutions of ammonium salts. In solutions of ammonium nitrate, magnesium dissolves rapidly, and after a time well-formed crystals of magnesium nitrate separate from the solution. Ammonium bromide attacks the metal with the simultaneous separation of the nearly insoluble magnesium bromide.

Magnesium Acetamide, $(CH_3CONH)_2Mg.4NH_3$. — When magnesium is added to a solution of acetamide the metal dissolves with the evolution of an equivalent amount of hydrogen. A clear, colorless solution is formed from which, after several hours, well-formed, colorless, granular crystals of magnesium acetamide containing 4 molecules of ammonia of crystallization separate. The salt is somewhat soluble in ammonia. It effloresces readily at laboratory temperature when the tube is opened and the ammonia is allowed to escape. When exposed to the air the dry salt absorbs water rapidly and forms a sticky mass, which does not dissolve completely in water but dissolves readily in hydrochloric acid.

I. 0.4577 gram crystallized salt lost 0.1443 gram NH_3.
0.3134 gram dry salt gave 0.2460 gram $Mg_2P_2O_7$.

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[1] This JOURNAL, 23, 304 (1900).

II. 0.5930 gram crystallized salt lost 0.1950 gram NH_3.
0.3980 gram dry salt gave 0.2960 gram $Mg_2P_2O_7$.

III. 0.2254 gram crystallized salt lost 0.0878 gram NH_3.
0.1376 gram dry salt gave 0.1092 gram $Mg_2P_2O_7$ and 0.0270 gram N.

IV. 0.2090 gram crystallized salt lost 0.0620 gram NH_3.
0.1406 gram dry salt gave 0.1045 gram $Mg_2P_2O_7$ and 0.0273 gram N.

	Calculated for $(CH_3CONH)_2Mg.4NH_3$.	Found. I.	II.	III.	IV.
NH_3	32.69	31.53	32.88	38.95[1]	29.67[2]

	Calculated for $(CH_3CONH)_2Mg$.	Found. I.	II.	III.	IV.
Mg	17.14	17.02	16.08	17.36	16.08
N	20.00	....	....	19.61	19.44

I. 0.0538 gram magnesum liberated 62.4 cc. hydrogen measured over water at 24° and 741 mm. barometric pressure.

II. 0.0692 gram magnesium liberated 77.4 cc. hydrogen measured over water at 27° and 740 mm. barometric pressure.

	Found for 1 equivalent of magnesium. I.	II.
H	1.08	1.04

Magnesium Benzenesulphonamide, $(C_6H_5SO_2NH)_2Mg.nNH_3$.—This compound is produced in the form of colorless crystals containing ammonia of crystallization when metallic magnesium is dissolved in an ammonia solution of benzenesulphonamide. The salt is slightly soluble. The effloresced salt gave the following analytical results.

0.1966 gram salt gave 0.0640 gram $Mg_2P_2O_7$ and 0.0159 gram N.

	Calculated for $(C_6H_5SO_2NH)_2Mg$.	Found.
Mg	7.28	7.05
N	8.39	8.11

Magnesium Cyanamide, $CNNMg.nNH_3$.—Cyanamide in solution in liquid ammonia immediately attacks metallic magnesium with the evolution of hydrogen gas. After a time the salt, which is moderately soluble, separates in the form of well-formed, granular crystals. The salt was recrystallized into the second arm of the apparatus, washed, and dried for analysis. The crystals contain ammonia of crystallization, as was shown by their efflorescence when the ammonia was allowed to escape. The crystals assumed a reddish tint on standing.

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[1] This specimen was known to contain an excess of ammonia.

[2] The salt was dried in a bath of ice and salt. The crystals showed distinct efflorescence.

0.0673 gram salt gave 0.02935 gram N.

	Calculated for $CNNMg$.	Found.
N	43.75	43.61

Summary of Results.

It has been shown in this investigation that the relation borne by the acid amides and the metallic amides toward liquid ammonia as a solvent is strikingly analogous to the well-known relations borne by the ordinary acids and bases to water.

Metathetic reactions between many acid amides and potassium amide in solution in liquid ammonia take place with all the facility which marks the interaction of ordinary acids and bases in aqueous solution.

Acid amides in solution in liquid ammonia attack potassium and sodium, and in some cases magnesium, with the evolution of hydrogen and the formation of the metallic derivatives of the acid amides.

The following salts have been prepared :

Monopotassium acetamide,
Monopotassium phenylacetamide,
Monopotassium benzamide,
Dipotassium benzamide,
Monopotassium benzenesulphonamide,
Dipotassium benzenesulphonamide,
Monopotassium toluenesulphonamide,
Monopotassium metamethoxybenzenesulphonamide,
Dipotassium metamethoxybenzenesulphonamide,
Monopotassium paramethoxybenzenesulphonamide,
Monopotassium sulphamide,
Dipotassium sulphamide,
Monopotassium urea,
Dipotassium urea,
Monosodium acetamide,
Magnesium acetamide,
Magnesium benzenesulphonamide,
Magnesium cyanamide.

In conclusion, the authors wish to express their appreciation of the kindness of Professor Arthur Lachman in placing the laboratories of the University of Oregon at their disposal for the prosecution of a portion of this work.

Laboratory of Physical Chemistry,
University of Kansas, Lawrence, Autumn, 1901.

Contributions from the Chemical Laboratory of the University of Vermont.

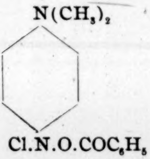
ON THE ACTION OF ETHYLENE DIBROMIDE ON PARANITROSODIMETHYLANILINE.

By Henry A. Torrey.

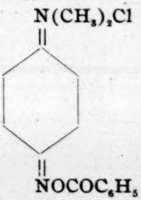
By heating ethylene dibromide with dimethylaniline at 100° C. for some time, Schoop[1] found that one of the hydrogen atoms in the ring was attacked and a dibenzyl derivative was obtained.

When the para position is occupied as in paranitrosodimethylaniline, the hydrogen of the ring is not attacked, a dibenzyl derivative is not obtained, but the nitroso group itself is acted upon, as is shown in the following study of the action of ethylene dibromide.

In a study of the action of benzoyl chloride on *p*-nitrosodimethylaniline, Ehrlich and Cohn[2] found that an addition-product is formed for which they give two possible formulas:



and



And Knorr,[3] by allowing a benzene solution of *p*-nitrosodimethylaniline and methyl iodide to stand for some time, obtained a similar addition-product, to which, on account of the nature of decomposition-products obtained by the action of sodium hydroxide, he assigns the formula:

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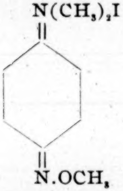
[1] Ber. d. chem. Ges., **13**, 2196.

[2] *Ibid.*, **26**, 1756.

[3] *Ibid.*, **30**, 933.



When ethylene dibromide acts upon nitrosodimethylaniline no such addition-product is obtained, although such a body may very likely be formed as an intermediate product. When *p*-nitrosodimethylaniline is warmed on the water-bath for a short time with a large excess of ethylene dibromide at least two products are obtained, the hydrobromide of *p*-nitrosodimethylaniline and a body consisting of 2 molecules of the base united by an ethylene residue. The reaction may be represented as follows:

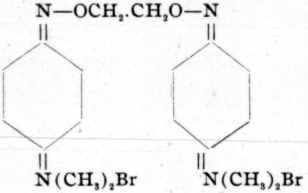
$$4NO.C_6H_4N(CH_3)_2 + BrCH_2.CH_2Br = \\ 2NO.C_6H_4N(CH_3)_2.HBr + [ON.C_6H_4.N(CH_3)_2]_2C_2H_2.$$

The identity of the *p*-nitrosodimethylaniline hydrobromide was proved by analysis and conversion into the free base by sodium carbonate.

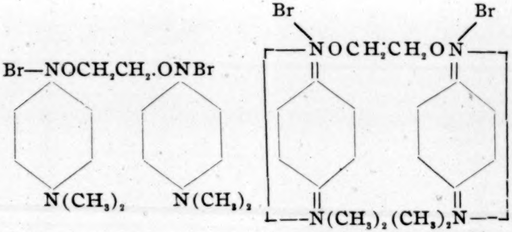
The second and more interesting product of the reaction, and which one may name dinitrosodimethylanilineethylene is a beautiful deep-red, crystalline compound, melting, with decomposition, at about 234° C.

That this product is not a dibenzyl derivative is shown by its great instability toward mineral acids, for although it is easily soluble in these acids it is impossible to recover the base by neutralization. Further, in his study of the formation of tetramethyldiamidodibenzyl by the action of ethylene dibromide on dimethylaniline, Schoop found that it was necessary to heat the mixture for eight days, while the action of ethylene dibromide on the less basic *p*-nitrosodimethylaniline is complete in as many minutes.

The most probable interpretation of the reaction is that the nitroso group is concerned in the reaction and that an addition-product is first formed, similar to those formed in the action of benzoyl chloride or methyl iodide, from which hydrobromic acid is split off, which is then taken up by the *p*-nitrosodimethylaniline which is still unacted upon. The ethylene dibromide might attach itself in three different ways, as follows :



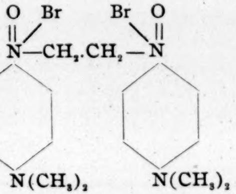
I.



Quinone formula.

II.

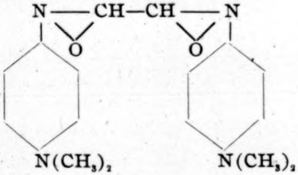
and



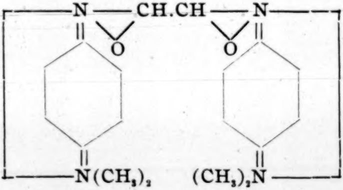
III.

III. may also, of course, be given the quinoid form.

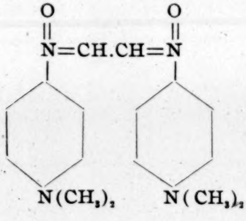
From a body having formula I. or II., by elimination of hydrobromic acid, a compound with the following formula would probably be obtained :



or

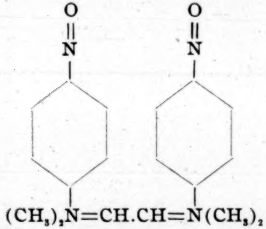


and III would give a body in which the nitrogen of the nitroso group is quinquivalent but that of the amino group trivalent, thus :



or in which, according to the quinone formula, both nitrogen atoms are quinquivalent.

That the union is not through the amino groups, thus,



is shown by the fact that the body, though easily broken down by mineral acids, still does form salts with some organic acids from which the original base can again be recovered by alkalies. With picric acid, for instance, a salt is obtained containing two equivalents of the acid, and which, by treatment with sodium hydroxide, gives the free body again.

The instability of this ethylene derivative toward small quantities of mineral acids is shown by the course of the reaction when it is carried on in alcoholic solution (85 per cent). Under these conditions the red dinitrosodimethylanilineethylene, which is first formed, is broken down, probably by the hydrobromic acid from partial hydrolysis of the hydrobromide of *p*-nitrosodimethylaniline, the nitroso groups are reduced at the expense of the hydrolyzed ethylene residue and tetramethyldiamidoazoxybenzene is formed, as is shown in the experimental part of this paper. That it is the salt of the nitrosodimethylaniline which brings about this decomposition in alcoholic solution is shown by the fact that when the red dinitrosodimethylanilineethylene is heated with *p*-nitrosodimethylaniline hydrochloride and alcohol the same reduction takes place, and tetramethyldiamidoazoxybenzene is formed, and that when it is heated with alcohol alone it is unchanged.

In studying the action of dilute mineral acids on the diparanitrosodimethylanilineethylene, it was found that dilute nitric acid was best adapted to this purpose, for by the use of this acid the separation of the different products of the reaction was facilitated, since the salt of paranitrosodimethylaniline, which is formed in this reaction, is, in the case of nitric acid, insoluble in water, while the other products remain in solution. The formation of *p*-nitrosodimethylaniline nitrate shows that the action of this reagent is partly hydrolytic, while the other products formed indicate that an oxidation of the ethylene residue and a reduction of the other nitrosodimethylaniline group have taken place. By neutralizing the filtrate from the nitrate a yellow body was obtained which melted at 255° to 256°, and contained no oxygen. The exact nature of this substance has not as yet been determined. The study of this body is being continued in collaboration with others in this laboratory. The filtrate from the yellow body responds to the tests for formic acid. The action of dilute nitric acid on diparanitrosodimethylanilineethylene is, therefore, a rather complex one. First of all, a partial hydrolysis takes place, the nitrate of *p*-nitrosodimethylaniline is formed and separates from solution, the other nitroso group is reduced at the expense of the hydrolyzed ethylene residue which is itself oxidized by the oxygen of the nitroso group and the nitric acid to formic acid.

EXPERIMENTAL PART.

Action of Ethylene Dibromide on Paranitrosodimethylaniline.

This reaction goes most smoothly when a large excess of ethylene dibromide is used. Forty grams of *p*-nitrosodimethylaniline were heated with 160 grams of ethylene dibromide for about six minutes on the steam-bath until the mixture had lost its green color and the reddish-brown reaction-product had separated copiously. It was then immediately cooled down and alcohol was added to stop the reaction, which is likely to become violent unless some such precaution is taken; or better, the mixture is kept at a temperature of 80° to 90° C., by alternate heating and cooling, and the reaction is allowed to go for a longer period (fifteen to twenty minutes). The mixture was then collected upon a filter, washed with alcohol, then with alcohol containing sodium hydroxide, and finally boiled out with alcohol and washed with ether. For further purification it was recrystallized from hot amyl alcohol, and washed with ethyl alcohol. By this treatment a beautiful garnet-red body, which crystallized in needles, was obtained. After drying in air, and finally in a desiccator, it was analyzed with the following results :

I. 0.1212 gram substance gave, on combustion, 0.2975 gram CO_2 and 0.0816 gram H_2O.

II. 0.1202 gram substance gave 0.2927 gram CO_2 and 0.0817 gram H_2O.

III. 0.1110 gram substance gave 0.2728 gram CO_2 and 0.0730 gram H_2O.

IV. 0.0992 gram substance gave 0.2419 gram CO_2 and 0.0640 gram H_2O.

V. 0.1512 gram substance gave 0.3662 gram CO_2 and 0.0934 gram H_2O.

VI. 0.1800 gram substance gave 27.0 cc. moist nitrogen at 20° C. and 761 mm. pressure.

VII. 0.1881 gram substance gave 29.6 cc. moist nitrogen at 25° C. and 753 mm. pressure.

	Calculated for	Found.						
	$(NO.C_6H_4N(CH_3)_2)_2C_2H_2$.	I.	II.	III.	IV.	V.	VI.	VII.
C	66.26	66.94	66.41	67.02	66.50	66.05	....	....
H	6.74	7.48	7.55	7.30	7.16	6.86	....	....
N	17.18	....	....	....	....	....	17.18	17.38

The body was found to contain no bromine. The analytical results show that the substance has the composition $C_{18}H_{22}N_4O_2$. As has been suggested earlier in this paper, it is most probable that the body is the result of the union of 2 molecules of *p*-nitrosodimethylaniline by means of an intermediate hydrocarbon group thus :

$$ON.C_6H_4N(CH_3)_2—C_2H_2—N(CH_3)_2C_6H_4.NO.$$

This substance may properly be called di-*p*-nitrosodimethylanilineethylene. The hydrobromic acid formed during the reaction is taken up by the free nitrosodimethylaniline present with the formation of the hydrobromide of this base. This body was separated from the reaction-mixture and identified as described below. The reaction of ethylene dibromide on *p*-nitrosodimethylaniline consists, thus, in the splitting off of 2 molecules of hydrobromic acid, the union of 2 molecules of the base with the ethylene residue and the subsequent formation of the hydrobromide of *p*-nitrosodimethylaniline, and may be expressed as follows :

$$4NO.C_6H_4N(CH_3)_2 + C_2H_4Br =$$
$$[NO.C_6H_4.N(CH_3)_2]_2C_2H_2 + 2NO.C_6H_4N(CH_3)_2HBr.$$

Properties of Di-p-nitrosodimethylanilineethylene.—The body crystallizes in deep-red needles from amyl alcohol, which decompose at 230° to 240° C., the temperature depending on the rapidity of the heating. It is soluble in chloroform and glacial acetic acid, very slightly soluble in ethyl alcohol and insoluble in water. It is very easily soluble in dilute mineral acids, by all of which, however, it seems to be decomposed. From its chloroform solution a well characterized picric acid salt was obtained. No precipitate was obtained when its aqueous hydrochloric acid solution was neutralized by sodium hydroxide or carbonate. It is reduced by zinc and acetic acid, and by sodium amylate in amyl alcohol solution; by treatment with the latter, one of the products formed is tetramethyldiamidoazoxybenzene, and this same body is obtained when it is heated with alcoholic *p*-nitrosodimethylaniline hydrochloride or when *p*-nitrosodimethylaniline itself is heated for a considerable time with alcoholic ethylene dibromide. Its chloroform solution gives a heavy black precipitate with a chloroform solution of iodine, and a rather gelatinous brown precipitate is given by a solution of bromine in chloroform. With very dilute nitric acid the body is broken down with the formation of *p*-nitrosodimethylaniline nitrate and a reduction-product, as will be described in another part of this paper.

p-Nitrosodimethylaniline Hydrobromide. — This substance was separated from the reaction-mixture by dissolving out the red ethylene derivative with glacial acetic acid, or better, with chloroform. After several crystallizations from methyl alcohol the substance was obtained in greenish-yellow crystals, somewhat darker in color than the hydrobromide which was prepared directly from the free *p*-nitrosodimethylaniline for comparison. The analyses, and its conversion into the platinum salt and into the free base leave no doubt, however, as to its identity. The body was dried in a desiccator and analyzed:

I. 0.1130 gram substance gave 0.1702 gram CO_2 and 0.0474 gram H_2O.

II. 0.1801 gram substance gave 19.9 cc. moist nitrogen at 17° C. and 743 mm. pressure.

III. 0.1303 gram substance gave 14.6 cc. N at 19°.25 C. and 742 mm. pressure.

IV. 0.1625 gram substance gave 0.1355 gram AgBr.

V. 0.1545 gram substance gave 0.1276 gram AgBr.

	Calculated for $C_6H_4NO.N(CH_3)_2HBr$.	Found. I.	II.	III.	IV.	V.
C	41.56	41.08	....	....	....	....
H	4.76	4.60	....	....	....	....
N	12.12	....	12.54	12.58	....	....
Br	34.72	....	....	....	35.48	35.14

Chlorplatinate.—For its further identification, the hydrobromide of the nitrosodimethylaniline, the analysis of which is given above, was treated with an excess of chlorplatinic acid dissolved in methyl alcohol. After allowing it to stand over night the crystalline precipitate was collected on a filter, washed with methyl alcohol and ether, and dried, in one case in the air and a vacuum desiccator, and in the second at 85° to 90° C. The analyses show the body to be the chlorplatinate of *p*-nitrosodimethylaniline.

I. 0.1478 gram salt gave, on ignition, 0.0406 gram Pt.

II. 0.1191 gram salt gave, on ignition, 0.0329 gram Pt.

	Calculated for $(NOC_6H_4N(CH_3)_2HCl)_2PtCl_4$.	Found. I.	II.
Pt	27.46	27.47	27.62

This is the same as the body which was obtained by the action of platinic chloride in methyl alcohol solution on the hydrochloride of nitrosodimethylaniline when dissolved in methyl alcohol, but it seems to be different from the platinum salts obtained by Schraube,[1] who mentions two salts, one having the formula $C_{16}H_{20}N_4O2HCl(PtCl_4) + H_2O$, and the other $C_{16}H_{20}N_4O.2PtCl_4 + H_2O$, which were obtained from dilute acid solution of the hydrochloride by adding platinic chloride in greater or less excess. When a great excess was added he obtained the second salt.

When chlorplatinic acid dissolved in methyl alcohol was added to a methyl alcohol solution of the hydrochloride of *p*-nitrosodimethylaniline the same platinum salt as described above was obtained.

To 1 gram hydrochloride of *p*-nitrosodimethylaniline dissolved in hot methyl alcohol 2.5 grams platinic chloride dissolved in methyl alcohol were added. A yellowish precipitate fell immediately, and the mixture was heated for a short time. This was collected on a filter, washed with methyl alcohol and ether, and dried for a short time at 90° C. The salt had a deep orange-red color. An analysis gave the following results:

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[1] Ber. d. chem. Ges., 8, 616.

0.3230 gram salt gave 0.0884 gram Pt on ignition.

	Calculated for $(NO.C_6H_4N(CH_3)_2HCl)_2PtCl_4$.	Found.
Pt	27.46	27.37

The filtrate, on standing, deposited well-shaped, deep-garnet crystals. These, on analysis, showed the same percentage of platinum:

0.0962 gram substance gave 0.0263 gram Pt, or 27.34 per cent.

Paranitrosodimethylaniline Hydrobromide.—This salt was also prepared directly by the addition of an aqueous solution of hydrobromic acid to *p*-nitrosodimethylaniline dissolved in methyl alcohol. A bright-yellow body crystallized out, which was collected on a filter, washed with alcohol, and dried in a vacuum desiccator over calcium chloride. On heating to 207° the salt decomposed.

0.1203 gram salt gave 0.0971 gram AgBr.

	Calculated for $NO.C_6H_4N(CH_3)_2HBr$.	Found.
Br	34.63	34.34

The same platinum salt as described above was obtained from this preparation of the hydrobromide. Before analysis it was crystallized from boiling water, washed with alcohol and ether, and dried at about 95° C.

0.1820 gram salt gave, on ignition, 0.0497 gram Pt.

	Calculated for $(NO.C_6H_4N(CH_3)_2HCl)_2PtCl_4$.	Found.
Pt	27.46	27.30

Action of an Alcoholic Solution of Ethylene Dibromide on Paranitrosodimethylaniline.

When *p*-nitrosodimethylaniline is added to an alcoholic solution of ethylene dibromide, and the mixture is heated to boiling for some time, the red ethylene derivative first formed is decomposed and the nitroso groups are partially reduced, and tetramethyldiamidoazoxybenzene is formed. Eight grams *p*-nitrosodimethylaniline, 18 grams ethylene dibromide, and 30 cc. alcohol (85 per cent), were heated on the steam-bath in a flask attached to a return-condenser for about one and one-fourth hours. The alcohol was then partly distilled off, the residue was allowed to cool, collected on a filter, washed with alcohol, and with sodium hydroxide and alcohol. The greenish-yellow product, crystallized from toluene, melted at 238° to 239° C. It dissolved in dilute sulphuric acid with a red color, and was precipitated as a bright yellow substance by sodium hydroxide. On reduction it gave dimethyl-*p*-phenylenediamine, which was identified by the methylene-blue reaction and isolation of the free base, which, after crystallization from benzene and ligroin, was obtained as colorless needles, melting at about 40° C.

The yield of the tetramethyldiamidoazoxybenzene was 3.1 grams. Analysis gave the following results:

I. 0.1184 gram substance gave 0.2975 gram CO_2 and 0.0815 gram H_2O.

II. 0.1580 gram substance gave 29.7 cc. N at 22°.5 C. and 744.5 mm. pressure.

	Calculated for $C_{16}H_{20}N_4O$.	Found.	
		I.	II.
C	67.60	68.52	....
H	7.04	7.65	....
N	19.72	....	20.79

If the alcoholic solution of ethylene dibromide and *p*-nitrosodimethylaniline is heated for only a short time, the conversion into tetramethyldiamidoazoxybenzene is by no means complete, and the red crystals of the diparanitrosodimethylanilineethylene may be seen in the reaction-mixture, especially after the hydrobromide has been removed by alcohol and sodium hydroxide.

When the red ethylene derivative itself is acted upon by the hydrochloride of *p*-nitrosodimethylaniline in boiling alcohol it is decomposed and the nitroso groups are reduced, just as above, to tetramethyldiamidoazoxybenzene.

Action of Acids on Diparanitrosodimethylanilineethylene.—This base dissolves easily in both dilute hydrochloric and sulphuric acids, but by neutralization with either sodium hydroxide or sodium carbonate it was impossible to obtain the original body again, and as yet no product of the action of these acids has been isolated and identified. With dilute nitric acid the reaction seems to go more smoothly, as will be described below. With picric acid in chloroform solution, which offered no opportunity for hydrolysis, a picrate was obtained.

To 5 grams of diparanitrosodimethylanilineethylene dissolved in chloroform, 8 grams of picric acid dissolved in chloroform were added. The solution at first turned purple, and then yellow crystals separated which were collected on a filter and washed with a very little chloroform, and finally with ether. The salt was freed from the solvent by allowing it to stand in the air, and finally in a desiccator over calcium chloride and paraffin. On long standing the salt shows a tendency to change from yellow to light-green on its surface. The salt gave the following result on analysis:

0.1040 gram substance gave 16.8 cc. N at 23° C. and 756.9 mm. pressure.

	Calculated for $[C_6H_4NO.N(CH_3)_2]_2C_2H_2.(C_6H_2(NO_2)_3OH)_2$.	Found.
N	17.86	18.13

A sample of the salt that had stood in the desiccator so long that it changed partially in color was also analyzed, but with the same result.

0.1616 gram substance gave 26.0 cc. N at 755.4 and 18° C., which corresponds to 18.47 per cent N.

The body is evidently the neutral diparanitrosodimethylanilineethylene picrate.

Properties of Picric Acid Salt.—This salt melts with decomposition at about 155° C. It is somewhat soluble in chloroform in the cold, giving a yellow solution, but only very slightly soluble in ether; in hot alcohol it dissolves with a red color, due to dissociation into the red base and free picric acid, and with warm water the free diparanitrosodimethylanilineethylene separates out as an insoluble body, the picric acid remaining dissolved. With a dilute solution of sodium hydroxide in the cold, the original base was separated from its salt, collected on a filter, and washed with water. It melted with decomposition at 225° without recrystallization.

Picric Acid Salt of Paranitrosodimethylaniline.—This salt was obtained by Schraube,[1] but it was not analyzed, neither were its properties given.

It is obtained as a yellow precipitate when 3 grams of picric acid dissolved in cold benzene are added to 2 grams *p*-nitrosodimethylaniline also dissolved in benzene. This was collected on a filter, washed with benzene, and allowed to dry in the air. After crystallizing from hot water and washing with alcohol, it was dried on a clay plate and finally in a desiccator over calcium chloride to constant weight. The following analytical results were obtained. For the determination of carbon and hydrogen it was found necessary to mix the substance with fine copper oxide.

	Calculated for $NO.C_6H_4N(CH_3)_2.C_6H_2(NO_2)_3OH$.	Found. I.	II.
C	44.32	43.93	....
H	3.43	3.84	....
N	18.47	....	18.62

Properties of Picric Acid Salt of Paranitrosodimethylaniline.—This salt crystallizes from water in rectangular plates. It decomposes at about 140°, showing signs of decomposition below this temperature. It dissolves in cold alcohol with a yellow color, is only slightly soluble in glacial acetic acid and chloroform, still less so in benzene, and is insoluble in ether. It is much more soluble in hot water than in cold. When treated with a sodium carbonate solution and shaken out with ether, the free *p*-nitrosodimethylaniline is obtained.

Action of Dilute Nitric Acid on Diparanitrosodimethylaniline-ethylene.—As has been mentioned above, this body is broken down when acted upon by mineral acids, even when very dilute. The products formed either by hydrochloric or sulphuric acid have not, as yet, been identified or isolated. With dilute nitric acid, however, the study of the reaction-products is simplified by the fact that one of these, the nitrate of nitrosodimethylaniline, being a much less soluble salt than either the hydrochloride or sulphate, is removed from the solution as soon as formed, while the other products remain in solution.

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[1] Ber. d. chem. Ges., 8, 616.

Five grams of the ethylene derivative were slowly added to 38 cc. of 15 per cent nitric acid diluted with 38 cc. of water. During the addition the mixture was constantly stirred and great pains taken to break up any lumps. The insoluble portion was collected on a filter and washed with a very little nitric acid of the same strength, and was purified by crystallization from a mixture of alcohol and water. After drying at about 95° C. it was analyzed with the following results:

I. 0.1147 gram substance gave 0.1919 gram CO_2 and 0.0577 gram H_2O.

II. 0.1048 gram substance gave 20.4 cc. N at 25° C. and 763 mm. pressure.

III. 0.1266 gram substance gave 24.4 cc. N at 28° C. and 744 mm. pressure.

	Calculated for $NO.C_6H_4N(CH_3)_2HNO_3$.	Found.		
		I.	II.	III.
C	45.07	45.63	....	....
H	5.16	5.59	....	....
N	19.71	....	20.69	21.64

The body is undoubtedly paranitrosodimethylaniline nitrate, since on treatment with sodium carbonate solution, and shaking out with ether, a green ethereal solution is obtained which deposits crystals melting at 85° to 86° (melting-point of paranitrosodimethylaniline, 85°). It was further identified by comparison with the nitrate made directly from an alcoholic solution of *p*-nitrosodimethylaniline and dilute nitric acid. Both salts melted with decomposition at 162°.

A determination of the nitrogen in the nitrate made directly, gave 20.48 per cent nitrogen.

The filtrate, when made alkaline with sodium carbonate, gave a reddish-yellow precipitate, which, after being washed with alcohol or ether, and crystallized from benzene, or better from alcohol, was obtained in the form of yellow plates (from alcohol), melting at 255° to 256°. This body dissolves with great ease in dilute mineral acids, giving a practically colorless solution, but in glacial acetic acid it dissolves with a blue color. Extremely dilute chloroform solutions of bromine and chlorine color its chloroform solution a beautiful deep-blue. It seems to contain no oxygen. The study of this body is being continued with others in this laboratory.

The filtrate from this yellow body was allowed to stand for some time, when a further precipitation occurred. This precipitate was filtered off and the alkaline filtrate, after shaking out with chloroform to remove the last traces of the yellow body, was examined. The almost colorless solution decolorized a mixture of potassium permanganate and dilute sulphuric acid, but gave no test for oxalates with calcium salts. It gave negative results for formic aldehyde with a decolorized fuchsin solution. Some of the solution was evaporated to dryness, the residue dissolved in dilute acetic acid, and tested for formic acid. It reduced silver nitrate easily on warming. The presence of formic acid was confirmed by the reddish precipitate given by another part of the solution which had been neutralized with dilute sulphuric acid and heated with ferric chloride, and by the precipitate of mercurous chloride given by heating with a solution of mercuric chloride.

I wish to express my gratitude to Mr. C. W. Whitney for his valuable assistance in a portion of the experimental work described in the first part of this paper.

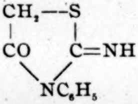
Contributions from the Sheffield Laboratory of Yale University.

XCVII.—ON THE MOLECULAR REARRANGEMENT OF THIOCYANACETANILIDES INTO LABILE PSEUDOTHIOHYDANTOÏNS; AND, ON THE MOLECULAR REARRANGEMENT OF THE LATTER INTO STABLE ISOMERS.

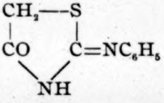
By Henry L. Wheeler and Treat B. Johnson.

Theory would require the existence of a large number of isomeric nitrogen-monosubstituted pseudothiohydantoïns, if mono-, bi-, and tricyclo combinations are considered, as well as stereoisomeric forms. But those chemists who have prepared these substances have invariably obtained, or recognized, only one form, even when methods have been employed which should yield isomers. In this and other respects the pseudothiohydantoïns behave in a tautomeric manner, and, therefore, the question of their structure has not been settled.

P. Meyer obtained phenylpseudothiohydantoïn not only from chloracetanilide and thiourea, but also from ethyl chloracetate and phenylthiourea, and from phenylthiohydantoic acid by warming with acetic acid.[1] He found that it gave N-phenyl-α,μ,diketotetrahydrothiazole (formula V.) when boiled with hydrochloric acid, and, therefore, he assigned the structure represented by formula I. to this compound. He also prepared the corresponding *p*-tolyl derivative.



I.



II.

Liebermann and Lange[2] then stated that monoalkylpseudothiohydantoïns might occur in two isomeric forms, formulas I. and II.; but on account of the formation of Meyer's thiohydantoïn from chloracetanilide he assumed that formula I. is correct. Soon after this Andreasch[3] prepared the same substance from phenylcyanamide and thioglycolic acid. He also concluded that of the two forms formula I. is the only one that can represent the structure of the compound. He assigned to the methyl and allyl derivatives a similar constitution.

This structure for phenyl and analogous pseudothiohydantoïns seems to have been accepted without question for fifteen years. To be sure, Neubert[4] gave to the phenylethyl analogue the form represented by formula II., and Goldschmidt and Gessner[5] also viewed the cumyl compound in a similar manner; nevertheless, no evidence in favor of this latter structure was offered.

[1] Ber. d. chem. Ges., **10**, 1965 (1877); **14**, 1661 (1881).

[2] Ann. Chem. (Liebig), **207**, 129 (1881).

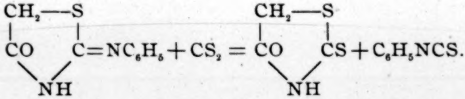
[3] Ber. d. chem. Ges., **15**, 325 (1882); Monatsh. Chem., **3**, 776 (1882); **6**, 840 (1885).

[4] Ber. d. chem. Ges., **19**, 1823 (1886).

[5] *Ibid.*, **22**, 933 (1889).

Finally, Dixon,[1] with the object of preparing isomeric pseudothiohydantoïns, investigated the action of chloracetylthiocarbimide on aniline, toluidine, etc. He found, however, that the same substances were formed by this as by other methods. He stated that "there can be no doubt that one thiohydantoïn alone is the product of interaction between (*a*) monosubstituted thiourea and ethylic chloracetate, (*b*) thiourea and substituted chloracetamide, (*c*) chlorinated acidic thiocarbimide and organic base." An experiment also showed that the same compound was formed by boiling thiohydantoïn with aniline.

He then examined the behavior of phenylthiohydantoïn with carbon bisulphide at a high temperature, and found that rhodanic acid (III.) was formed. This was the first evidence produced in favor of formula II. for phenylthiohydantoïn and its analogues. Dixon states that the reaction took place as follows:



III.

This, however, did not settle the structure of the compounds in question, since it left unexplained not only the formation of N-phenyl-α,μ-diketotetrahydrothiazole (formula V. below) by boiling with hydrochloric acid, but also the fact that isomers are not obtained by other methods, especially that of Andreasch, the synthesis from thiourea and substituted chloracetamide, and the fact that it can be prepared from thiocyanacetanilide by boiling with alcohol.

Rizzo[2] stated that chloracetanilide and ammonium thiocyanate give thiocyanacetanilide, $NCSCH_2CONHC_6H_5$, melting at 176°, but Frerichs and Beckurts[3] found this compound to be the long-known phenylthiohydantoïn of P. Meyer.

Meanwhile, W. Grothe[4] had just described a series of compounds which he believed were normal thiocyanacetanilides. Frerichs and Beckurts repeated the work and concluded that by the action of potassium thiocyanate on chloracetanilide there first results the rhodanacetanilide described by Grothe as melting at 86° to 87°. On heating an alcoholic solution of this rhodanide, they found that Meyer's phenylthiohydantoïn was produced.

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[1] J. Chem. Soc. (London), **71**, 620 (1897).

[2] Centrbl., 1898, II., 296.

[3] Arch. Pharm., **238**, 615 (1900).

[4] *Ibid.*, **238**, 610 (1900).

The latter authors then undertook the examination of Grothe's compounds, in order to determine whether they are normal or isothiocyanates. They believed their results to show that, with the exception of rhodanacetmethylanilide, the substances are normal thiocyanates. Then followed the description of an interesting experiment which was, however, incorrectly interpreted. They stated, but without producing any proof for the structure of the compounds, that when potassium thiocyanate acts on chloracetparatoluide, in alcoholic solution, for only a short time, a labile compound results, which they considered to be isothiocyanacettoluide,

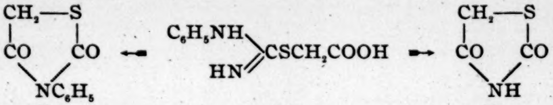
$$SCN—CH_2CONHC_6H_4CH_3.$$

They observed that when this solution was warmed the compound was rapidly converted into a substance which they supposed was normal thiocyanacettoluide,

$$NCSCH_2CONHC_6H_4CH_3,$$

and the latter was finally changed into paratolylthiohydantoïn. This brings us to the point where our work commenced.

We first found that the structure of phenylpseudothiohydantoïn cannot be determined by boiling the compound with hydrochloric acid. Not only is N-phenyl-α,μ-diketotetrahydrothiazole (V.)[1] formed but also α,μ-diketotetrahydrothiazole ("Senfoelessigsäure," formula VI.), which latter substance has been overlooked by previous workers.



V. IV. VI.

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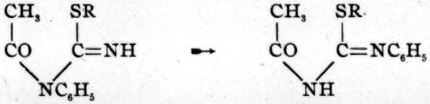
[1] That formula V., represents the structure of this compound and not that assumed by Dixon was shown by Wheeler and Barnes: This JOURNAL, 24, 64 (1900).

Under this treatment, therefore, the compound behaves in a tautomeric manner. This is undoubtedly to be explained by the assumption that a saponification of the cyclic amide takes place, phenylthiohydantoic acid (IV.) is first formed, and this then condenses and decomposes with the above results.

In view of the fact that the pseudothiohydantoïns are cycloacylpseudothioureas, the same molecular rearrangement should be met with in this series as in the corresponding acyclic cases.

In a previous article[1] it has been shown by us that unsymmetrical acetylphenylpseudothioureas, as well as the corresponding acylthioureas, readily undergo a metastatic change into the symmetrical derivatives, as follows :



VII. VIII.

On comparing these structures with those represented by formulas I. and II., it will be noticed that Meyer's structure I. corresponds to the labile acyclic form VII., while the formula of Dixon is analogous to the acyclic stable acetylphenylpseudothiourea (VIII.).

Since we found, in our previous work, that the labile acylpseudothioureas are too unstable to be crystallized from alcohol without undergoing a molecular rearrangement, the observations of Frerichs and Beckurts seemed to point to a similar state of affairs in the case of the thiohydantoïns. Moreover, it was shown by Wheeler and Merriam[2] that rhodanacetmethylanilide, contrary to the statement of Frerichs and Beckurts, is not an isothiocyanate. This rendered doubtful the correctness of their assertion that rhodanacetparatoluide first gives an isothiocyanate. It also seemed highly improbable that normal thiocyanacetanilide undergoes a direct molecular rearrangement into the stable hydantoïn of Dixon, without first forming a hydantoïn having the structure suggested by Meyer and others. We therefore undertook the preparation of rhodanacetanilides according to Grothe's directions, and were not unprepared for the interesting results which followed.

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[1] This Journal, 27, 270 (1902).

[2] J. Am. Chem. Soc., 23, 297 (1901).

In the first place, we found that although the phenyl, the orthotolyl, and the paraxylyl compounds are correctly described as rhodanides, on the other hand, the so-called rhodanacetparatoluide and rhodanacetparaphenetidide are neither normal nor isothiocyanates. The paratolyl compound is, in fact, a representative of the missing labile pseudothiohydantoïns, which, for the present, can be represented by Meyer's formula (I.). Dixon's formula (II.), on the other hand, is to be assigned to the long-known phenylthiohydantoïn, a similar one to Grothe's rhodanacetparaphenetidide and to the stable thiohydantoïns previously obtained.[1]

In the second place, the molecular rearrangement of thiocyanacetanilide into the stable hydantoïn does not involve an isothiocyanate at any stage, but proceeds precisely as our previous work would indicate.

(*a*) When chloracetanilide and potassium thiocyanate are dissolved in strong alcohol and warmed about a half hour, a mass of colorless prisms, which melt at about 91°, separate on cooling. This, the first substance formed, is normal thiocyanacetanilide (IX.).

(*b*) When the above compound, in the dry state, is melted on the steam-bath for fifteen minutes, it is converted into an isomeric substance. This melts at 148° and can be crystallized repeatedly from benzene and also from strong alcohol. It is the missing phenylpseudothiohydantoïn (X.).

(*c*) When the above labile products are heated much longer than fifteen minutes on the steam-bath, or for a few minutes at a higher temperature, or boiled for a short time with dilute alcohol, they are transformed, with partial decomposition, into the stable hydantoïn of P. Meyer and others, melting at 178° (XI.).

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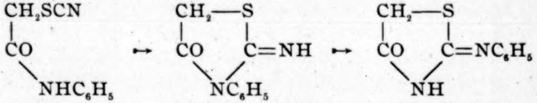
[1] Those pseudothiohydantoïns with the aliphatic groups, methyl and allyl, may be exceptions. In all probability, however, the formulas given to the thiohydantoïns from rhodanacetylthioureas and rhodanacetylurethane (Arch. Pharm., **238**, 319 (1900)) should be revised. This subject will receive attention at a later time.

We have also obtained each of the three products directly, by boiling alcoholic solutions of chloracetanilide and potassium thiocyanate under slightly different conditions, and we have prepared the corresponding ortho- and paratolyl and paraxylyl derivatives. The low temperature, less than 100°, at which the metastatic changes can be produced, is noteworthy.



M. P. 91°. IX. M. P. 148°. X. M. P. 178°. XI.

The facts on which the above statements in regard to the structure of the three products are based are as follows:

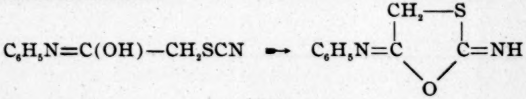
(*a*) The material melting at 91° was shown to be a normal thiocyanate by warming it in benzene with thioacetic acid, whereupon not more than traces of hydrogen sulphide were given off and a thiol ester was obtained, namely,

$$CH_3CO.SCH_2CONHC_6H_5.$$

There can be no doubt as to the structure of this compound, since we have also prepared it from sodium thioacetate and chloracetanilide.

(*b*) The compound melting at 148°, on treating as above with thioacetic acid, evolved hydrogen sulphide and an acetyl derivative resulted. This behavior towards thioacetic acid shows that the substance is neither a normal nor an isothiocyanate, and since it appears to be the first condensation-product of thiocyanacetanilide it can be represented by formula X.

The possibility must also be considered that this labile compound is a derivative of the unknown furothiole ring (XII.). The condensation would then involve the pseudoform of the anilide as follows:



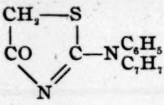
XII.

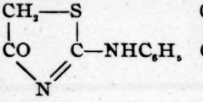
These latter structures, however, for the labile products are excluded, since they are not reconcilable with the ease with which the labile hydantoïns are decomposed into hydantoic acids and substituted cyanamides (see below). This behavior also excludes the possibility that this type of thiohydantoïns has an isomeric structure similar to the isothiohydantoïn of Miolati,[1] which would result if the condensation was analogous to that of the rhodanacetones[2] or to that of orthocyanbenzoic acid.[3]

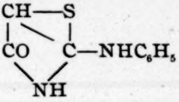
(*c*) The stable thiohydantoïn has the structure assigned to it by Dixon (formula XI.), because unsymmetrical benzylphenylthiourea,

$$H_2N—CS—N(C_6H_5)CH_2C_6H_5,$$

and ethylchloracetate give the same compound as is obtained by treating the stable thiohydantoïn with alkali and benzyl chloride (formula XIII.). This proves that the phenyl group is attached to nitrogen outside the ring, but it does not determine the position of the hydrogen which has been replaced by the benzyl group. If it did, the stable thiohydantoïn would have the structure represented by formula XIV., or some such structure as XV.


XIII.


XIV.


XV.

Formula XIV. represents a compound insoluble in alkali and, therefore, is excluded. Formula XV. is also excluded by the fact that the above benzylphenylthiohydantoïn is insoluble in alkali. The most probable structure for the stable pseudothiohydantoïns is, therefore, that represented by formula XI. This agrees not only with the solubility of the compound in alkali and ammonia but it also corresponds to that structure required for the formation of rhodanic acid. It contains the hydrogen atom in the most probable position, as indicated by the direction[1] of metastatic change in the case of the acylthioureas, and it best explains the fact that the compound is not acetylated by thioacetic acid.[2]

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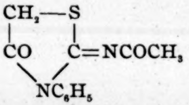
[1] Chem. Centrbl., 1893, I., 641.

[2] Hantzsch and Weber: Ber. d. chem. Ges., **20**, 3127; Arapides: Ann. Chem. (Liebig), **249**, 20.

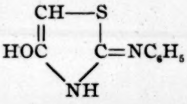
[3] Sandmeyer: Ber. d. chem. Ges., **18**, 1499; Kuhara: This JOURNAL, **3**, 26; Auger: Ann. chim. phys., [6], **22**, 289; Hoogewerff and Van Dorp: Rec. trav. chim. Pays-Bas, **11**, 91 (1892).

The fact that benzyl chloride gives a compound having the structure represented by formula XIII. is therefore a satisfactory confirmation of the view, expressed several years ago by one of us,[3] that in the alkylation of amidines by means of alkyl halides, the alkyl group does not necessarily directly replace hydrogen, but that in certain cases, if not in general, it unites with a doubly bound nitrogen, $=NR$, in preference. At any rate, the position of hydrogen attached to nitrogen in these cases cannot be determined by alkylation or substitution.[4]

The acetyl derivative mentioned above, which results on warming the labile hydantoïn with thioacetic acid, is identical with the product obtained by the action of acetic anhydride on phenylthiohydantoic acid. It also results when thiocyanacetanilide is warmed with acetic anhydride. From the latter synthesis and the fact that the compound exhibits no tendency to undergo a molecular rearrangement, we conclude that its structure is to be represented by formula XVI. Such an acetyl derivative would be expected from a labile hydantoïn having the structure represented by formula X.



XVI.



XVII.

On the other hand, the stable thiohydantoïn, which is not acted on by thioacetic acid, reacts in a peculiar manner with acetic anhydride and a diacetyl derivative results. The product is insoluble in cold alkali, and, on warming, the stable thiohydantoïn is recovered. It follows from this that the hydrogen of the methylene group is not directly replaced by one or both acetyl groups. If, as sometimes maintained, the position of hydrogen in tautomeric substances can be determined by acetylation, the structure of the stable thiohydantoïn would therefore be represented by some such formula as XVII., XVIII, XIX., or XX.

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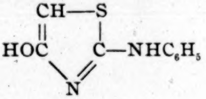
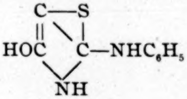
[1] This Journal, **27**, 274 (note).

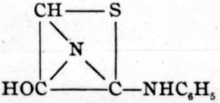
[2] Compare Näf: "On Amidothiazoles," Ann. Chem. (Liebig), **265**, 108 (1891).

[3] This Journal, **20**, 482 (1898).

[4] Compare Knorr: Ber. d. chem. Ges., **28**, 708 (1895); Wislicenus: Ann. Chem. (Liebig), **312**, 61 (1900); Michael: Ber. d. chem. Ges., **33**, 3740 (1901); J. prakt. Chem., **46**, 204; **60**, 324 (1899).


XVIII.


XIX.


XX.

But these formulas are excluded since diphenyl and the above benzylphenylpseudothiohydantoïn are insoluble in alkali. Moreover, Mr. G. S. Jamieson, working in this laboratory, has found that the methylene hydrogen in the stable hydantoïn is capable of reacting with aldehydes and other substances[1] in a similar manner to that of benzyl cyanide.[2] A like behavior had been previously observed by Andreasch in the case of the non-substituted thiohydantoïn,[3] and by others[4] in dealing with compounds which contain the —CO—CH_2—S— group.

It follows from these results that acetylation, like alkylation, cannot be relied on to determine the position of hydrogen in the pseudothiohydantoïns.

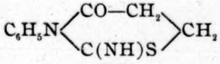
[1] These reactions will be described in a later paper.

[2] V. Meyer: Ann. Chem. (Liebig), **250**, 124 (1889).

[3] Monatsh. Chem., **8**, 407.

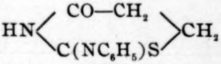
[4] Loven. Ber. d. chem. Ges., **18**, 3242 (1885); Nencki and Sieber: *Ibid.*, **17**, 2278 (1884); Ginsberg and Bondzynski: *Ibid.*, **19**, 119 (1886); Monatsh. Chem., **8**, 358 (1887); Andreasch: *Ibid.*, **8**, 407, **10**, 75 (1889).

Since in the stable thiohydantoïns the aryl group is outside the ring, it follows also that a corresponding six-membered ring structure described by Langlet[1] as 3-phenyl-2-imino-4-acitetrahydro-1,3-azthin (formula XXI.), prepared from phenylthiourea and β-iodopropionic acid, should undoubtedly be represented by formula XXII. In other words, the compound in question is 2-phenylimino-4-acitetrahydro-1,3-azthin:



$$C_6H_5N\left\langle\begin{matrix}CO-CH_2\\C(NH)S\end{matrix}\right\rangle CH_2$$

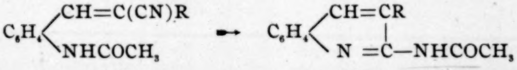
XXI.



$$HN\left\langle\begin{matrix}CO-CH_2\\C(NC_6H_5)S\end{matrix}\right\rangle CH_2$$

XXII.

A molecular rearrangement analogous to ours, inasmuch as a cyanogen group and an amido group condense to produce a ring and the resulting compound then undergoes a further rearrangement, was observed by Pschorr[2] in the case of α-arylorthoacetaminocinnamic nitriles. These compounds, under the influence of dilute alkali or acids, are transformed into α-acetamino-β-arylquinolines, the result being expressed as follows:



$$C_6H_4\left\langle\begin{matrix}CH=C(CN)R\\NHCOCH_3\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}CH=CR\\ \quad\;\; |\\N=C-NHCOCH_3\end{matrix}\right.$$

Pschorr and Wolfes state that in this metastatic change no intermediate products could be obtained, and therefore the mechanism was not explained.

In regard to the mechanism of the metastatic changes represented above, by formulas IX., X., and XI., that involved in the first step requires no further consideration. The second molecular rearrangement can be accounted for by the assumption that the labile product (X.) condenses to form a compound having the structure represented below either by formula XXIII. or XXIV. A simple shifting of the bonds, along with hydrogen in the first instance, will then give the structure required by the stable hydantoïn.

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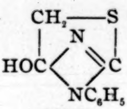
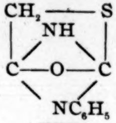
[1] Beilstein's Handbuch: Spl. Bd. II., 200 (Privatmittheilung).

[2] Ber. d. chem. Ges., **31**, 1289 (1898); Pschorr and Wolfes: *Ibid.*, **32**, 3399 (1899).



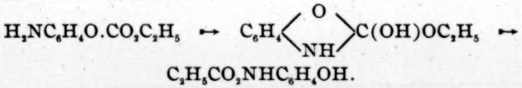
XXIII.



XXIV.

The bicyclo formula (XXIII.) represents an intermediate, inner addition-product, analogous to the intermediate product commonly assumed in the case of the saponification of acid and imino esters by amines,[1] and which was shown by us to exist in the thionurethane series.[2] According to this we have a case of intramolecular saponification similar to Willstätter's "intramolekulare Alkylirung.[3]

A compound having this structure would be analogous to the hypothetical intermediate product by means of which Ransom[4] explains the molecular rearrangement of aminophenylethyl carbonate into oxyphenylurethane :



$$H_2NC_6H_4O.CO_2C_2H_5 \rightarrow C_6H_4{<}\substack{O\\NH}{>}C(OH)OC_2H_5 \rightarrow C_2H_5CO_2NHC_6H_4OH.$$

A similar intermediate product may be considered to have at least a momentary existence in the case of the molecular rearrangement of orthoamidobenzylacetparatoluide into orthoacetamidobenzylparatoluidine, and possibly a like one also during the rearrangement of unsymmetrical diarylsemicarbazides,[5] although Widman,[6] who described the former change, states that a third product was not observed.

These molecular rearrangements are probably due to the fact that the acyl group has a tendency to migrate to the most positive position in the molecule, and in the above manner the system may avoid a concentration of negative groups.

Formula XXIII. might therefore, without objection, be as-

[1] Stieglitz : This Journal, **21**, 107 (1899).

[2] *Ibid.*, **24**, 191 (1900).

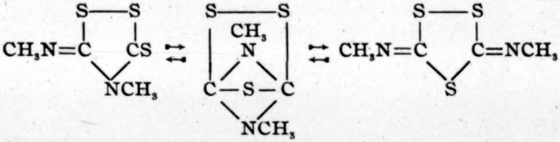
[3] Ber. d. chem. Ges., **34**, 139 (1901).

[4] This Journal, **23**, 11 (1900).

[5] Busch and Holzmann : Ber. d. chem. Ges., **34**, 320 (1901).

[6] J. prakt. Chem., **47**, 354 (1893).

signed to the intermediate product were it not for the interesting, but hitherto unexplained, observation of Walther and Stenz[1] that "phenylparatolylsulfhydantoïn" occurs in two forms, one melting at 113°, the other at 169°, and that the lower-melting substance can be transformed into the higher. Evidently, in this case no such bicyclo combination as XXIII. is possible. If this is actually a molecular rearrangement like ours then the intermediate product can have a tricyclo structure similar to that represented by formula XXIV. In the same manner the reversible molecular rearrangement described by Freund[2] can be explained, in which 1-methyl-2-methylimino-5-thio-3,4-disulphazolidin changes into 2,5-dimethyliminodimethylenetrisulphide and *vice versa*.



The possibility, however, is not excluded that the mechanism of the molecular rearrangement of disubstituted thiohydantoïns is different from that of the mono derivatives and that the intermediate product in the latter case has the enol structure (XXIII.). Indeed, our experiments do not exclude the possibility that the labile thiohydantoïn itself has this structure. This view receives support from the fact that the labile phenylthiohydantoïn gives a wine-yellow color in the cold with ferric chloride, while the rhodanide and the stable thiohydantoïn do not. Moreover, in the case of the orthotolyl derivatives the labile thiohydantoïn gives the stable isomer on treating with cold alkali, while the thiocyanate, under similar treatment, gives orthotolylcyanamide. In order to give a cyanamide, the rhodanide must first condense to form a compound with the structure represented by formula X., but this is the structure first assigned to the labile hydantoïn. On the other hand, the labile phenylthiohydantoïn and the rhodanide both give phenylthiohydantoic acid.

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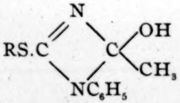
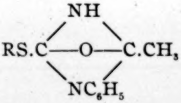
[1] J. prakt. Chem., 61, 576 (1900).

[2] Ann. Chem. (Liebig), 285, 138 (1895).

This behavior of the labile products with alkali points decidedly to the conclusion that there are three metastatic changes involved in this molecular rearrangement and two structurally different labile thiohydantoïns. This question and whether the structure of the labile thiohydantoïns that have been isolated is correctly represented by formula X., XXIII., or XXIV. will require further work to decide, and, therefore, we hope to continue the present investigation with especial consideration of these problems at the opening of the next college year.

Either formula XXIII. or XXIV. will explain the mechanism not only of the rearrangement in question, but also that of the acylthioureas, the reaction being a monomolecular one, involving an inner condensation. In the latter case the intermediate product can be represented by one of the following formulas:





Bicyclo combinations, more or less analogous to XXIII., are now being assigned to a number of compounds. Michaelis[1] advances the formula XXV. for antipyrin[2] and its sulphur and selenium analogues, while Busch has recently obtained a series of substances which, as he believes, have a similar structure.[3] Interesting in this respect are the corresponding urazole and the isomeric forms of the thiourazoles of Marckwald and Sedlaczek,[4] which, according to Busch,[5] exhibit tautomerism in the sense illustrated by formulas XXVI. and XXVII. The thiourazoles corresponding to these formulas undergo a reversible rearrangement, as shown by the arrows:

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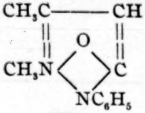
[1] Ann. Chem. (Liebig), **320,** 2 (1902).

[2] A structure previously considered but not accepted by Knorr: *Ibid.*, **293,** 26, (1896).

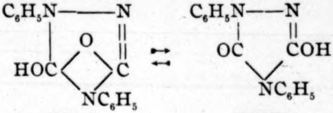
[3] Ber. d. chem. Ges., **34,** 326 (1901).

[4] *Ibid.*, **29,** 2920 (1896).

[5] *Ibid.*, **35,** 975 (1902).



XXV.



XXVI. XXVII.

The thiocyanacetanilides and the labile thiohydantoïns, which we have examined, cannot be boiled for any length of time with aqueous alcohol, water, acetic acid, or the like, without more or less readily undergoing decomposition and rearrangement into the stable form. This, and their behavior on heating, explains why the various methods hitherto employed have given only one form of pseudothiohydantoïns. In addition to the above molecular rearrangement, the labile pseudothiohydantoïns readily undergo hydrolysis. A saponification or rupture of the ring takes place immediately on treating with cold alkali, or even on warming for a short time with dilute alcohol.

Three reactions have been observed on treating the thiocyanacetanilides and the labile hydantoïns with cold alkali: (*a*) A molecular rearrangement into the stable form; (*b*) the formation of thiohydantoic acids; (*c*) a decomposition into substituted cyanamides and thioglycolic acid.

The stable thiohydantoïns, on the other hand, exhibit considerable stability towards alkali, forming crystalline sodium salts, from solutions of which acetic acid precipitates the unaltered material. This fact was observed in the case of stable phenylpseudothiohydantoïn by previous workers.

The behavior of the cyclo derivatives, both with heat and with alkali, is therefore analogous to that of the corresponding acyclic acylthioureas, and it is an interesting fact that the ring structure of the pseudothiohydantoïns confers no especial stability on the labile products and does not interfere with this now general molecular rearrangement.

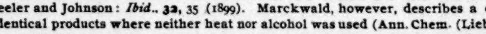
It can be stated in regard to the ease with which the labile pseudothiohydantoïns undergo molecular rearrangement that they are more closely allied to the labile unsymmetrical acylthioureas than to the labile acylpseudothioureas. The former acyclic compounds can be easily crystallized from alcohol while the latter cannot, without undergoing a metastatic change. Under certain conditions the labile pseudothiohydantoïns can be crystallized from alcohol, and, in fact, even the thiocyanacetanilides, which are less stable than the labile thiohydantoïns, can be submitted to this treatment.

The homologues of thiocyanacetanilide appear to be more stable than the prototype. However, in all cases care must be taken to avoid prolonged warming, especially in dilute alcohol. Grothe makes no mention of this nor of the formation of thiohydantoïns, thiohydantoic acids, etc. With the exception of rhodanacetparaphenetidide, which was submitted to the violent treatment of being crystallized from acetic acid and consequently gave the stable hydantoïn, all the others were apparently crystallized from dilute alcohol.

In connection with the behavior of our labile compounds with solvents and heat, it is noteworthy that in deciding the identity of products in the case of the amidines, when prepared by methods which should yield isomers, crystallization from alcohol has almost invariably been resorted to before the melting-point of one specimen would coincide exactly with that of the other.[1]

Finally, in concluding this introduction, it must be stated that the molecular rearrangement of the pseudothiohydantoïns and that described by Freund are not the only cases observed in which an alkylimino group within a cyclo structure has been found to undergo a metastatic change to a position outside the ring, or *vice versa*.

Rathke[2] observed a closely analogous case to that of ours among the phenylmelamines, in which the group $=NC_6H_5$ changes places with a $=NH$ group:



$$=\overset{|}{C}-(NC_6H_5)-\overset{|}{C}=NH \longleftrightarrow =\overset{|}{C}-NH-\overset{|}{C}=NC_6H_5.$$

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[1] Pechmann: Ber. d. chem. Ges., **28**, 869, 2363 (1895); **30**, 1779, 1783 (1897); Wheeler and Johnson: *Ibid.*, **32**, 35 (1899). Marckwald, however, describes a case of identical products where neither heat nor alcohol was used (Ann. Chem. (Liebig), **286**, 355 (1895)). Mercaptan, however, was present and the reaction required many days before it was complete. Compare also Hantzsch and Perkin on diazoamino compounds, Ber. d. chem. Ges., **30**, 1394 (1897).

[2] Ber. d. chem. Ges., **21**, 867 (1888).

Pinner[1] found that the normal oxygen hydantoïns, under the influence of alkali, undergo a transformation into pseudohydantoïns. In this case an oxygen atom and an imino group shift positions:

$$R\overset{|}{C}H—NH—\overset{|}{C}O \mapsto R\overset{|}{C}H—O—\overset{|}{C}{=}NH.$$

The molecular rearrangement of the isoimides into normal imides described by Hoogewerff and Van Dorp,[2] Van der Meulen,[3] Kuhara and Fukui,[4] is another example of a metastatic change that takes place, in all probability, in a similar manner to that of ours:

$$O\overset{|}{C}—O—\overset{|}{C}{=}NH \mapsto O\overset{|}{C}—NH—\overset{|}{C}O.$$

It is noticeable that in these labile compounds there exists a combination of unsaturated groups, residual affinity or double bonds, the latter usually on each side of a bivalent group. This condition is favorable for a change in the manner in which the atoms are united and therefore significant of the mechanism of these curious molecular rearrangements.[5]

EXPERIMENTAL PART.

The products which we have obtained by boiling alcoholic solutions of potassium thiocyanate with the chloracetanilides have been examined in regard to their behavior towards thiolacids and alkali, and also on heating. In the case of the orthoxylyl compounds a lack of material rendered it impossible to make a thorough examination. For the same reason rhodanacetphenetidide was not isolated. The reactions have served to determine whether the compounds in question are normal thiocyanates, labile or stable thiohydantoïns, as indicated in the introduction. It need only be further remarked that the action of thioacetic and thiobenzoic acids on this series of rhodanides is by no means as simple as that usually observed in the case of monothiocyanates.[6] It appears that if about the calculated quantity of thio acid is used, the conditions are favorable for the formation of a thiol ester; if an excess, either an acetyldithiourethane or a simple dithiourethane results; frequently all three of these compounds. The formation of a simple dithiourethane, which involves the addition of hydrogen sulphide to the rhodanide, has hitherto been observed in this reaction, only in the case of methylene and ethylene rhodanides.[1] In some experiments, on crystallizing the product of the reaction from alcohol, nothing but the stable hydantoïns were obtained. Besides these compounds, more or less sticky varnishes accompany the products, and hydrogen sulphide and cyanogen, or hydrogen cyanide, are evolved. Carbon disulphide was not observed. There are, therefore, no isothiocyanates to be considered.

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[1] Ber. d. chem. Ges., **22**, 686 (1889).

[2] Rec. trav. chim. Pays-Bas., **12**, 12 (1893); **13**, 93 (1894).

[3] *Ibid.*, **15**, 282.

[4] This JOURNAL, **26**, 454 (1901).

[5] Compare Lapworth: "On a Possible Basis of Generalization of Intramolecular Changes in Organic Compounds," J. Chem. Soc. (London), **73**, 445 (1898).

[6] J. Am. Chem. Soc., **23**, 283 (1901); This JOURNAL, **26**, 345 (1901).

The melting-, decomposing-, or effervescing-points of the thiohydantoic acids which we describe are not definite. They seem to depend not only on the purity of the sample but also on the rate and manner of heating. In this respect they behave in the same way as phthalic acid and other compounds which decompose or lose water on heating.[2] The melting-points given for these acids are, therefore, only approximate.

Normal Thiocyanacetanilide, $NCSCH_2CONHC_6H_5$. — We have usually obtained this compound when 5 to 10 grams of chloracetanilide were boiled with a slight excess of potassium thiocyanate in 30 cc. of alcohol (95 per cent or absolute), for twenty to thirty minutes. If larger quantities of the chloride are taken it frequently happens that nothing but the labile hydantoïn is obtained. With 30 grams, for example, it is difficult to get the chloride completely acted upon before the formation of the second labile product begins. After the reaction is over, the addition of a little water to the cooled solution causes a mass of fine, colorless, needle-like prisms to separate. These, under the usual conditions of a melting-point determination, melt at about 91°. If slowly heated, they melt below this temperature. On heating very rapidly they have been observed to melt as high as 94°. Nitrogen determinations gave:

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[1] Wheeler and Merriam: J. Am. Chem. Soc., **24**, 440 (1902).

[2] Remsen: This JOURNAL, **3**, 30 (1881); Wheeler: *Ibid.*, **18**, 830 (1896); Bancroft: J. Phys. Chem., **3**, 74 (1899).

	Calculated for $C_9H_8ON_2S$.	Found.	
		I.	II.
N	14.58	14.44	14.64

If an attempt was made to recover the material from the mother-liquors, especially by adding water and then evaporating, a mixture consisting essentially of phenylthiohydantoic acid and the stable thiohydantoïn was obtained. These latter compounds were obtained directly when chloracetanilide and potassium thiocyanate were warmed in dilute alcoholic solution.

When the rhodanide is crystallized from alcohol it forms plates, but the melting-point is lowered to about 86° to 88°. Grothe gives 86° to 87°. When crystallized from benzene, especially if the solutions are dilute, large, thin, transparent plates or scales, like mica, are obtained, which, on exposure to the air, show a decided change in appearance. The first evidence of change begins along the edges of the crystals ; an etching appears, which deepens and spreads until the entire specimen becomes opaque and the colorless material changes to a white mass. The transparent crystals show no sharp melting-point but start to melt at a little above 60° and are completely melted at 83°. At a higher temperature they effervesce explosively. On standing about an hour, however, they melt more sharply at 87° to 88°. It was found that the transparent crystals contain benzene of crystallization, which is rapidly lost on heating or exposure.

The confusing behavior of this substance in regard to melting-point and on crystallizing, together with the fact that in the thioacetic acid reaction various results were obtained, since over four compounds seem to be formed under apparently the same conditions, led us at first to believe that we had to deal with two substances, a rhodanide, melting at about 91°, and a labile thiohydantoïn, melting at 87°. It was only after a number of experiments, in which it was found that similar results could be obtained with a variety of these products, that this view was abandoned.

Action of Thioacetic Acid.—Two grams of the rhodanide, melting at 90° to 91°, and one gram of thioacetic acid in 10 cc. of dry benzene, were heated for two and a half hours on the steam-bath. The benzene was then removed by evaporation and the residue, washed with dilute sodium hydroxide, was taken up in ether and allowed to crystallize by spontaneous evaporation. On recrystallizing from alcohol colorless, needle-like prisms were obtained which melted at 97° to 98°, and a nitrogen determination agreed with the calculated for acetylthioglycollanilide, $CH_3CO.SCH_2CONHC_6H_5$:

	Calculated for $C_{10}H_{11}O_2NS$.	Found.
N	6.69	6.72

The structure of this compound was established by the fact that the same substance is formed immediately on mixing a warm solution of chloracetanilide in alcohol with sodium thioacetate. When the material thus obtained was mixed with some of the above, it was found that the melting-point was not altered.

Two experiments as above, with thioacetic acid and products melting at about 88°, gave material which, on crystallizing from alcohol, formed the stable hydantoïn.

It happened twice that when 2 grams of the labile product, melting at about 87° and 91°, were heated for two hours in 20 cc. of benzene, with an equal weight of thioacetic acid, that some difficultly soluble material was formed, which crystallized from alcohol in fine, hair-like needles and melted with decomposition at 192°. This product was in all probability an acetyldithiourethane, but there was not obtained a sufficient amount for examination and analysis. The chief product formed in these cases was the thiol ester described above.

In other experiments we obtained the following result: Eight grams of the labile product were heated in 60 cc. of benzene with 7 grams of thioacetic acid for two and a half hours. On cooling then, fine, colorless, crystalline material separated, which formed square plates from alcohol and melted at 162°, showing slight decomposition. Nitrogen and sulphur determinations agreed with the calculated for the dithiourethane, $H_2NCS.SCH_2CONHC_6H_5$:

	Calculated for $C_9H_{10}ON_2S_2$.	Found.
N	12.3	12.1
S	28.3	28.4

In accordance with this, the material dissolves in alkali and suffers decomposition, forming alkali thiocyanate and the sodium salt of thioglycollanilide. Hydrogen chloride precipitates material melting at 107° to 108° (thioglycollanilide[1]).

Action of Alkali.—Both the products melting at 88° and 91° dissolve immediately in cold sodium hydroxide, and carbon dioxide thereupon throws down a colorless crystalline precipitate, practically insoluble in alcohol, which melts at about 185° to 190° with decomposition and effervescence. A nitrogen determination agreed with the calculated for phenylthiohydantoic acid, $C_6H_5N{=}C(NH_2)SCH_2COOH$:

	Calculated for $C_9H_{10}O_2N_2S$.	Found.
N	13.33	13.41

Behavior on Heating: Labile Phenylpseudothiohydantoïn.—A sample of the rhodanide, which melted at 90° to 91°, was melted in a capillary tube and cooled; on reheating it showed no signs of melting until the temperature reached 136° to 140°. When larger quantities are melted for a few minutes on the steam-bath, then crystallized from benzene, beautiful, square tables result which melt at 148°, forming a blood-red liquid. When quickly cooled from a mixture of benzene and petroleum ether the material forms acicular crystals. This labile product, unlike the rhodanide, can be repeatedly crystallized from strong alcohol; however, when boiled with dilute alcohol, phenylthiohydantoic acid and the stable hydantoïn result. The latter is also formed when the labile products are allowed to remain too long at a temperature of 100°. Nitrogen determinations in the case of the tables melting at 148° agreed with the calculated for α-keto-μ-imino-N-phenyltetrahydrothiazole:

	Calculated for $C_9H_8ON_2S$.	Found. I.	Found. II.
N	14.58	14.90	14.42

The crystallography of the labile phenylpseudothiohydantoïn melting at 148° and also that of the stable phenylpseudothiohydantoïn was investigated by Mr. Paul C. Condit under the direction of Professor S. L. Penfield. We take this occasion to express our thanks for the work. The crystals of the labile phenylpseudothiohydantoïn selected for measurement were obtained by crystallizing the material from strong alcohol. They were transparent, had a pale-yellow color, and looked like cubes, having a diameter of about 2 mm.

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[1] Rizzo: Centrbl., 1898, II., 296.

Their crystallization, however, is orthorhombic and the forms usually observed were only the prisms, $m = 1,1,0$ and the basal planes, $c = 0,0,1$. In some cases domes occurred, $d = 0,1,1$. The habit is shown in Fig. I. The faces were badly etched, especially the *c* faces. The character of these etchings on the basal planes, which were parallel to the diagonals, is shown in Fig. II.

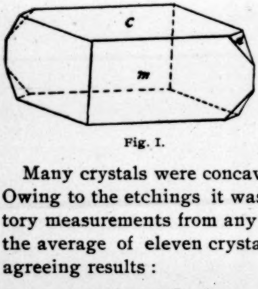

Fig. I.

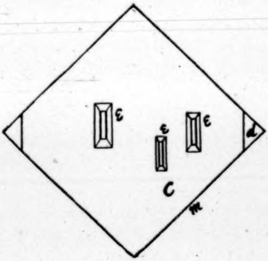

Fig. II.

Many crystals were concave on the upper and lower faces. Owing to the etchings it was not possible to obtain satisfactory measurements from any one crystal, and those given are the average of eleven crystals which gave the most closely agreeing results :

$m \wedge m' = 87^\circ 44'$; $m \wedge m''' = 92^\circ 0'$;

$d \wedge d' = 53^\circ 12'$; $m \wedge c = 90^\circ 0'$.

The axial ratio is :

$$a : b : c : : 0.97 : 1 : 1.35.$$

In polarized light the crystals showed a bi-axial interference and an extinction direction parallel to the diagonals ; the cleavage is also parallel to the diagonals.

The *hydrochloride*, obtained by treating a benzene solution of the labile phenylpseudothiohydantoïn with dry hydrogen chloride, melts with effervescence at 192° to 193°. A nitrogen determination gave :

	Calculated for $C_9H_9ON_2ClS$.	Found.
N	12.25	12.38

The *picrate* separates in bright-yellow prisms from alcohol and melts at 180°.

Action of Thioacetic Acid.—When the material melting at 148° was warmed in benzene with thioacetic acid, hydrogen sulphide was evolved in quantity. The product was then crystallized from alcohol, whereupon colorless, needle-like prisms were obtained, which melted at 191° to 192°. We also prepared this acetyl derivative by three other methods, namely, by the action of acetic anhydride on both of the labile products and on phenylthiohydantoic acid. The rhodanide readily dissolves in cold acetic anhydride while the labile hydantoïn does not, and to effect acetylation it is necessary to warm the solutions in both cases for some time on the water-bath. A nitrogen determination gave results agreeing with the calculated for α-keto-μ-acetimido-N-phenyltetrahydrothiazole :

	Calculated for $C_{11}H_{10}O_2N_2S$.	Found.
N	11.96	12.00

Action of Alkali.—The labile phenylthiohydantoïn dissolves in cold sodium hydroxide to form a light-yellow solution, from which carbon dioxide precipitates phenylthiohydantoic acid.

Behavior on Heating : Stable Phenylpseudothiohydantoïn.—When the labile hydantoïn melting at 148° is melted in a capillary tube and heated to 165° the material undergoes the next metastatic change, since, when cooled and reheated, it melts at a higher temperature. The transformation of the above labile compounds, and also their analogues, into the stable hydantoïn, by heat, is invariably accompanied by more or less decomposition. The material assumes a reddish-brown color, even when the change is produced by prolonged heating at 100°. In this case, if the temperature does not exceed 150° to 155°, the decomposition-products are easily extracted by boiling with benzene, and pure phenylpseudothiohydantoïn is left as a difficultly soluble residue, melting at 178°.

It is noteworthy that while the stability of the compounds in this series increases from the rhodanide to the stable hydantoïn, the solubility diminishes. For the preparation of the stable hydantoïns in quantity, the method of P. Meyer, which consists in boiling the hydantoic acids with acetic acid, is most convenient.

The crystals of the stable phenylthiohydantoïn belong to the triclinic system. Those obtained for measurement were about 2 mm. in length and were formed in alcoholic solution. The forms observed were $a = 0,1,0$; $b = 1,0,0$; $c = 0,0,1$; $d = 1,0,1$; $M = 1,1,0$. The majority of crystals showed only the pinacoids, *a* and *b*, and the dome, *d*. The habit is shown in Figs. III. and IV.

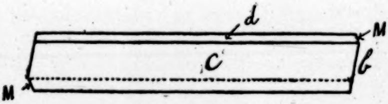

Fig. III.

Nearly all the crystals were twinned in a complicated manner and it was not possible to obtain any satisfactory results under the microscope. The average results of many measurements were as follows:

$a \wedge b$ 78° 51′; $b \wedge c$ 77° 53′; $a \wedge c$ 64° 56′;
$a \wedge d$ 108° 52′; $b \wedge m$ 39° 33′.

From this

$\alpha = 108° 25'$; $\beta = 113° 15'$; $\gamma = 96° 35'$.

The axial ratio is:

$$a : b : c :: 1.508 : 1 : 0.859.$$

The crystals showed a cleavage parallel to the base.

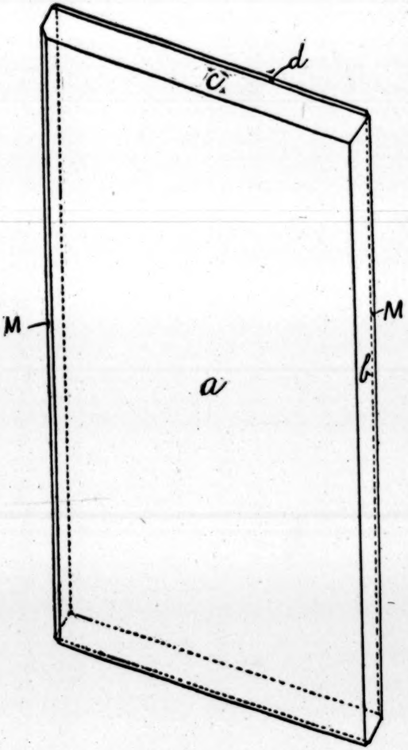

Fig. IV.

Action of Acetic Anhydride.—No reaction was observed to take place when the stable phenylpseudothiohydantoïn was heated with thioacetic acid in boiling benzene. When it was dissolved in acetic anhydride and warmed for a few hours on the steam-bath, a solution resulted which deposited no crystals on cooling. The addition of water then produced a precipitate which crystallized from benzene in flat prisms and melted at 161° to 162°. When mixed with the above acetyl derivative, melting at 163°, which was obtained from the labile monocyclohydantoïn and thioacetic acid, the melting-point was lowered to 135° or 140°. Nitrogen determinations agreed with the calculated for a diacetyl derivative:

	Calculated for $C_{13}H_{12}O_3N_2S$.	Found.		
		I.	II.	III.
N	10.1	10.3	10.2	10.0

This compound is insoluble in cold dilute alkali, but on warming it dissolves and acetic acid precipitates the stable hydantoïn. Quantitative determinations of the acetyl groups were made by boiling the material with standard potassium hydroxide and then titrating the excess of alkali with hydrochloric acid.

Calculated for $(CH_3CO—)$.	Calculated for $(CH_3CO—)_2$.	Found.	
		I.	II.
18.3	31.1	35.4	35.0

This diacetyl derivative was also obtained by warming the stable hydantoïn in benzene with an excess of acetyl chloride (Analysis III. above). Under these conditions the hydrochloride of the hydantoïn is also obtained.

The *stable phenylpseudothiohydantoïn hydrochloride* can be crystallized from alcohol. It then forms colorless needles which melt at 203° with decomposition and effervescence. It is insoluble in benzene.

Action of Alkali and Benzyl Chloride.—When the stable hydantoïn is treated with dilute sodium hydroxide it dissolves, and suddenly a mass of colorless plates of the sodium salt separate. This can be crystallized from boiling water. Carbon dioxide or acetic acid then liberates the unaltered hydantoïn. Five and a half grams of the stable hydantoïn were warmed on the steam-bath with the calculated quantity of sodium dissolved in dilute alcohol and a slight excess of benzyl chloride. After the alkaline reaction had disappeared the alcohol was evaporated and the residue, when washed with alkali, taken up in ether, and crystallized from alcohol, gave beautiful square tables which melted at 124° to 125°. The same material was obtained from unsymmetrical benzylphenylthiourea, $C_6H_5.CH_2(C_6H_5)N—CS—NH_2$, and ethyl chloracetate by proceeding in the usual manner. The crystals thus obtained had the same melting-point as the above and when samples of the two were mixed the melting-point was not lowered. Dixon gives the melting-point of this hydantoïn at 118° to 119° (corr.).

Normal Thiocyanacetorthotoluide, $NCSCH_2CONHC_6H_4CH_3$.—When chloracetorthotoluide was boiled for ten to thirty minutes, in alcoholic solution, with potassium or ammonium thiocyanate, a compound resulted which, on crystallizing from dilute alcohol, formed colorless needles that melted at 102° to 103°, as stated by Grothe. When this material was suspended in ether, in which it is very difficultly soluble, and warmed for two hours, the material, when simply washed, then melted at about 109°. The same effect was produced when the product melting at 102° to 103° was crystallized a number of times from benzene. The long needle-like crystals then had a more prismatic habit. Both these products behaved in the same manner towards thioacetic acid.

Action of Thioacetic Acid.—About 2 grams of the material and 1 gram of thioacetic acid, freshly distilled over phosphorous sulphide, were mixed in 7 cc. of benzene that had been boiled over sodium. The mixture was boiled for one hour, and then, on evaporating the benzene and treating the brown varnish, thus obtained with ether, material separated which proved to be very difficultly soluble in alcohol, and, on boiling, it remained as a sandy, white powder ; a portion separated from the solution in the form of needles. The material melted with effervescence to a deep-brown liquid near 200°. It had all the properties of a dithiourethane, and a nitrogen determination indicated that the substance is an acetyldithiourethane, $CH_3CONHCSSCH_2CONHC_6H_4CH_3$:

	Calculated for $C_{12}H_{14}O_2N_2S_2$.	Found.
N	9.9	10.6

Action of Thiobenzoic Acid.—The material was better characterized as a rhodanide by means of thiobenzoic acid. The treatment was the same as with thioacetic acid. Colorless or pale-yellow material was obtained which crystallized from alcohol in long needles that melted at about 141° to 142°. A nitrogen determination showed that this is benzoylthioglycoll-orthotoluide, $C_6H_5CO.SCH_2CONHC_6H_4CH_3$:

	Calculated for $C_{16}H_{15}O_2NS$.	Found.
N	4.9	5.41

There can be no doubt in regard to the structure of this compound since we have also prepared the substance from the chloride and potassium thiobenzoate. The material melting at 109° or at 102° to 103° is therefore a normal thiocyanate.

Action of Alkali.—The rhodanide was dissolved in cold alkali and acetic acid then precipitated an oil which readily solidified. On crystallizing from alcohol and ether, in which the material was very soluble, colorless prisms, melting at 77°, were obtained. This material was free from sulphur and proved to be identical with orthotolylcyanamide described by Voltmer.[1]

Behavior on Heating: Labile Orthotolylpseudothiohydantoïn.—Although the rhodanide melts at 109° under the usual conditions of a melting-point determination, and on remelting, practically the same fusing-point is noticed, nevertheless, it can be melted by warming for a half hour on the steam-bath. It then forms a brown tar on cooling. If heated for a sufficient time, crystals of stable orthotolylpseudothiohydantoïn separate. An attempt was made to avoid the formation of this tar by heating in boiling toluene, and for this purpose 3 grams of the material were dissolved in 10 cc. of the solvent and boiled for five minutes; on cooling, unaltered material separated which melted at 109°. On evaporating the toluene on the steam-bath nothing but a brown-black tar and crystals of the stable hydantoïn were obtained.

[1] Ber. d. chem. Ges., **24**, 381.

Finally it was found that a labile product intermediate between the rhodanide melting at 109° and the stable body melting at 144° to 145°, could be prepared as follows, although the yield is poor on account of the formation of decomposition-products. A little over 7 grams of the air-dried rhodanide were heated to 110° in an oil-bath for thirty minutes. During this process a quantity of material sufficient for a melting-point determination sublimed in colorless needles. It melted at 109° and was therefore the unaltered substance. When the brown mass was extracted with benzene about 0.3 gram of an insoluble product was obtained. This melted at 222° with effervescence and proved to be orthotolylthiohydantoic acid. The benzene filtrate, on spontaneous evaporation, deposited small, lozenge-shaped crystals, which were purified by warming with small quantities of benzene. The colorless material thus obtained, about a gram, on rapidly heating in a capillary tube, melted at 131° to 132° and quickly crystallized again, even when the temperature was maintained above 132°. It then refused to melt completely until heated to 142° to 145°. This intermediate product appears to be less stable than the corresponding phenyl compound. Although it can be crystallized from benzene, nevertheless, on continued warming in this solvent it is converted into the stable hydantoïn. It dissolves on gently warming with dilute alkali, and acetic acid precipitates the stable hydantoïn.

Stable Orthotolylpseudothiohydantoïn, for purposes of comparison, was prepared from orthotolylthiourea and chloracetic acid. It crystallized in two forms, long needles and stout tables, and both forms melted at 144° to 145° as stated by Dixon, and when mixed with the final product of the above molecular rearrangement, the melting-point was not lowered. In passing, it may be remarked that orthotolylthiourea was observed to melt at 162° and not at 155°, the melting-point given by Staats.[1]

Action of Acetic Anhydride.—When the stable hydantoïn was warmed on the steam-bath with acetic anhydride a solution was obtained from which water precipitated an oil. On standing some time the material solidified, and when crystallized from alcohol it formed stout, six-sided tables, which melted at 91° to 92°. It is very soluble in benzene and insoluble in cold alkali. The analysis gave results agreeing with the calculated for a diacetyl derivative :

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[1] Ber. d. chem. Ges., **13**, 136 (1880).

	Calculated for $C_{14}H_{14}O_3N_2S$.	Found.
N	9.66	9.95

Orthotolylthiohydantoic Acid.—This was obtained in one attempt to prepare the labile hydantoïn. Four grams of chloracetorthotoluide and 3 grams of potassium thiocyanate were dissolved in 30 cc. of alcohol and heated for a half hour on the steam-bath. On adding water nothing but a turbidity resulted. The solution was then concentrated, whereupon a colorless, insoluble, white powder separated. It formed small, thin plates and decomposed with effervescence between 208° and 230°. A nitrogen determination gave :

	Calculated for $C_{10}H_{12}O_2N_2S$.	Found.
N	12.50	12.68

On further concentrating the solution stable hydantoïn was obtained.

Normal Thiocyanacetparatoluide, $NCSCH_2CONHC_6H_4CH_3$.—When chloracetparatoluide and potassium thiocyanate are boiled in alcoholic solution for a short time and the mixture that results is crystallized from absolute alcohol or benzene, it forms needle-like prisms and the melting-point of the product appears to be constant at about 85°.

Action of Thioacetic Acid.—The material was heated with thioacetic acid for forty-five minutes in benzene solution. On distilling the benzene and testing for carbon disulphide not a trace was found. The substance, therefore, is not an isothiocyanate. On the other hand, by the Prussian-blue test, hydrogen cyanide was found to be present. The chief product formed, however, was not a thiol ester, but it had all the properties of a dithiourethane. Nitrogen and sulphur determinations agreed with the calculated for the compound $CH_3C_6H_4NHCOCH_2S.SCNH_2$:

	Calculated for $C_{10}H_{12}ON_2S_2$.	Found.
N	11.66	11.92
S	26.66	25.88

Behavior on Heating.—A specimen of the rhodanide, which melted at about 85°, began to solidify at 86°. It was heated a few degrees higher and then cooled. On reheating, it did not melt completely until at about 120°. When the material was melted on the steam-bath for a few minutes and then crystallized from absolute alcohol it formed colorless needles which melted at 125° to 126°, the melting-point previously found for the rhodanide. This latter material is:

Labile Paratolylpseudothiohydantoïn.—This results when the solutions of the chloride and potassium thiocyanate are warmed on the water-bath for a half hour.

Action of Thioacetic Acid.—A portion of the crude labile hydantoïn was warmed in benzene with thioacetic acid. Hydrogen sulphide was evolved in quantity and, on cooling, crystals separated. On crystallizing from alcohol beautiful, colorless plates were obtained which melted at 175° to 176°. That this was neither a thiol ester nor a dithiourethane was shown by the fact that the same acetyl derivative resulted on warming the labile hydantoïn with acetic anhydride. A nitrogen determination gave:

	Calculated for $C_{12}H_{12}O_2N_2S$.	Found.
N	11.29	11.12

Action of Alkali.—The labile hydantoïn dissolved in cold alkali and carbon dioxide, then precipitated a cream-colored, crystalline powder, which was insoluble in water, very difficultly so in alcohol, and which decomposed at about 210° to 212°, with effervescence. A nitrogen determination gave results agreeing with the calculated for paratolylthiohydantoic acid:

	Calculated for $C_{10}H_{12}O_2NS$.	Found.
N	12.50	12.21

Behavior on Heating.—When the material melting at 125° is melted in a capillary tube and cooled it gives a varnish.

If not heated too much or too long it can be solidified and then remelts at 125°. Several grams of the labile hydantoïn, which, after one crystallization from benzene, melted at 121°, were dried and warmed on the steam-bath. In a few minutes the material became colored and in a half hour it was mostly melted. The heating was continued for a half hour longer, whereupon, on cooling, the brown mass readily solidified and an odor of hydrogen cyanide or cyanogen was present. The material was now difficultly soluble in benzene and on simply boiling with this solvent pure, stable paratolylpseudothiohydantoïn, melting at 183°, was left as a residue, while the benzene solution contained the varnish-like impurities that were formed during the metastatic change. When the labile hydantoïn was heated in an oil-bath at temperatures near its melting-point for a short time, a deep-brown mass was obtained, which, on crystallizing from benzene, melted incompletely at about 175°. The question whether this product contains a new isomer or is simply impure stable hydantoïn must be decided later. It is interesting to note also that a change into the stable hydantoïn, accompanied by the formation of a brown coloring-matter, can be brought about in a few hours on exposing this high-melting labile hydantoïn to a temperature as low as 75°.

The *stable paratolylpseudothiohydantoïn*, obtained as above, or by concentrating the aqueous alcoholic filtrates from the labile derivatives, formed needles from alcohol which melted at 183°, as stated by P. Meyer. On treating this material with alkali it was converted into a mass of thin plates or lozenge-shaped spangles of the sodium salt, which, with acetic acid, gave unaltered hydantoïn.

Action of Acetic Anhydride.—The stable hydantoïn was warmed on the water-bath with an excess of acetic anhydride for about an hour and a half. Water then precipitated material which crystallized from alcohol in the form of pale-yellow prisms melting at 163° to 164°. A nitrogen determination gave a result agreeing with the calculated for a diacetyl derivative :

	Calculated for $C_{14}H_{14}O_3N_2S$.	Found.
N	9.66	10.00

Labile α-Orthoxylylpseudothiohydantoïn (?).—The orthoxylidine was prepared by nitrating 50 grams of orthoxylene with a mixture of 50 grams of red fuming and 400 grams of ordinary concentrated nitric acid at 10°. The yield of nitroxylene, boiling at 163° to 173° at 50 mm. pressure, was 25 grams. When the xylene is nitrated with red, fuming[1] nitric acid alone, little or no mononitroxylene is obtained. The nitro compound was reduced with tin and hydrochloric acid in the usual manner. When the chloracetyl derivative of this amine was treated with potassium thiocyanate, as in the case of the phenyl compound, and the product was crystallized from benzene, colorless plates were obtained which, instead of melting at 103° as stated by Grothe, melted at 111°.

Action of Thioacetic Acid.—Three grams of the labile xylylhydantoïn were warmed for about a half hour in benzene with thioacetic acid. The benzene, on evaporating, left a varnish which was washed with water and crystallized from dilute alcohol, whereupon pale-yellow needles were obtained, which melted at 179°. This material was soluble in alkali and was reprecipitated unaltered by acetic acid. A nitrogen determination agreed with the calculated for the stable hydantoïn, α-keto-μ-α-orthoxylyliminotetrahydrothiazole :

	Calculated for $C_{11}H_{12}O_2N_2S$.	Found.
N	12.74	12.81

α-Orthoxylylthiohydantoic Acid.—On concentrating the filtrates from the preparation of the labile hydantoïn and warming the residue with water, some insoluble, colorless, minutely crystalline material was obtained which was observed to melt at about 208° with effervescence and decomposition. A nitrogen determination gave :

	Calculated for $C_{11}H_{14}O_3N_2S$.	Found.
N	11.76	11.64

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[1] Jacobson states fuming acid (Ber. d. chem. Ges., 17, 160).

Normal Thiocyanacetparaxylidide, $NCSCH_2CONHC_6H_3(CH_3)_2$ $CH_3,NH,CH_3,1,2,4$.—The xylidine employed was isolated from commercial material by means of the excellent method of Hodgkinson and Limpach.[1] The chloracetyl derivative melted at 153°. When this was boiled with potassium thiocyanate for a half hour in alcoholic solution, the crystals that separated melted at 125°–129°. On recrystallizing from alcohol they melted at a lower temperature. From the mother-liquor more was obtained by adding water. This melted less sharply at 118° to 124°, but on drying and crystallizing from benzene it formed colorless plates and melted at 133°, the melting-point previously assigned to this rhodanide. Some of the material melting at 125° to 129° was dissolved in alcohol and evaporated to dryness on the water-bath. It then melted at 120° to 130°. On repeating this treatment it still melted at about 120° to 125°. It was then boiled for two hours in strong alcohol, whereupon, on evaporating to dryness, a thick varnish was obtained from which the stable hydantoïn melting at 161° to 162° separated on treating with benzene.

Action of Thioacetic Acid.—About 2 grams of the material melting at 125° to 129° were heated with a slight excess of thioacetic acid in 10 cc. of benzene for little over an hour. Very little hydrogen sulphide was given off, and on cooling beautiful, colorless prisms separated which, when crystallized from alcohol, melted at 139° to 140°. A nitrogen determination agreed with the calculated for acetylthioglycollparaxylidide, $CH_3CO.SCH_2CONHC_6H_3(CH_3)_2$:

	Calculated for $C_{12}H_{15}O_2NS$.	Found.
N	5.90	5.83

Action of Alkali.—Some of the material melting at 125° to 129° was dissolved in cold, normal sodium hydroxide. Acetic acid then precipitated a colorless, crystalline powder, which formed flat prisms from dilute alcohol and melted, when further purified by recrystallizing from a mixture of benzene and petroleum ether, at 118°. This material was free from sulphur, and nitrogen determinations agreed with the calculated for paraxylylcyanamide, $C_6H_3(CH_3)_2NH—CN$:

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[1] J. Chem. Soc. (London), 77, 65.

	Calculated for $C_9H_{10}N_2$.	Found. I.	Found. II.
N	19.17	18.91	19.16

Behavior on Heating.—Not only is this rhodanide most stable in solvents but also when heated in the dry state. On melting in a capillary tube it forms a varnish. A portion was heated on the steam-bath and it required two hours or more to obtain the material in a completely melted condition. On crystallizing the black varnish thus obtained from benzene a small amount of unaltered rhodanide, which melted at 131° to 133°, was recovered. A slight residue, insoluble in benzene, proved to be paraxylylthiohydantoic acid, while from the benzene solution, on further concentration, crystals of the stable hydantoïn separated.

Labile Paraxylylpseudothiohydantoïn.—The rhodanide was converted into a compound that appears to be the labile hydantoïn by boiling in dry ether for one or two hours. The material remained mostly undissolved, and then, on crystallizing from benzene, beautiful needles separated which melted constantly at 109° to 110°. A nitrogen determination gave:

	Calculated for $C_{11}H_{12}ON_2S$.	Found.
N	12.72	12.84

Action of Thioacetic Acid.—Although the rhodanide reacts readily with thioacetic acid, on the other hand, the labile hydantoïn can be boiled in benzene for hours without giving much evidence of a reaction. After warming more than twenty-four hours the product was a mixture. It melted at 105° to 114° and under the microscope it was seen to consist of needles and prisms. We did not succeed in purifying this material by crystallizing from benzene, and further attempts were abandoned. When the labile hydantoïn is treated with alkali it gives paraxylylcyanamide.

Paraxylylthiohydantoic acid, $C_6H_3(CH_3)_2N(H_2N)CSCH_2COOH$, was obtained, mixed with brown decomposition-products, when the alcoholic solutions from the rhodanide were diluted with water and evaporated on the steam-bath. It was purified by boiling with alcohol, in which it only partially dissolved. It then decomposed at about 200° with effervescence. A nitrogen determination gave:

	Calculated for $C_{11}H_{14}O_2N_2S$.	Found.
N	11.76	11.94

When this acid was dissolved in alkali it gave *p*-xylylcyanamide.

Stable Paraxylylpseudothiohydantoïn.—The alcoholic extracts from the above hydantoic acid were evaporated to dryness on the steam-bath. From the brown residue material was obtained which crystallized from a mixture of benzene and petroleum ether in the form of minute prisms, and melted at 161° to 162°. A nitrogen determination gave:

	Calculated for $C_{11}H_{12}ON_2S$.	Found.
N	12.72	12.65

This hydantoïn is quite soluble in alcohol. It dissolves in normal sodium hydroxide and can be precipitated unaltered by carbon dioxide.

The paraphenetidine employed in the following experiments was prepared from paranitrophenetol by reduction with tin and hydrochloric acid. The nitration of phenetol was accomplished by dissolving three parts of the material in a mixture of 2 parts of red, fuming nitric acid and 16 parts of ordinary concentrated nitric acid, the whole being kept at a temperature of 5° to 15°. On diluting with ice-water and washing, the liquid orthonitrophenetol was removed by pressing on a vacuum filter. The paranitrophenetol boiled at 146° at 11 mm. pressure. The rhodanide in this case was not obtained in a pure condition.

Labile Paraphenetylpseudothiohydantoïn.—A crude product, obtained by boiling an alcoholic solution of chloracetparaphenetidide with potassium thiocyanate for a short time, and which melted at 100° to 115°, was dried and crystallized from benzene. It then melted constantly at 128°. A nitrogen determination gave:

	Calculated for $C_{11}H_{12}O_2N_2S$.	Found.
N	11.8	12.1

Another crude product, melting at 95° to 110°, was suspended in ether and boiled. This procedure gave the same compound, melting at 128°.

Action of Thioacetic Acid.—When the labile hydantoïn was warmed in benzene solution with thioacetic acid, hydrogen sulphide was evolved. The product formed needles or prisms from alcohol and melted at 155°. A nitrogen determination agreed with the calculated for a monoacetyl derivative :

	Calculated for $C_{13}H_{14}O_3N_2S$.	Found.
N	10.00	10.26

Behavior on Heating.—When the labile hydantoïn is melted in a capillary tube and slowly cooled it solidifies. On reheating it shows no signs of melting at 128°, but melts at about 151° to 155° to a deep-red liquid. A portion was melted in an oil-bath at 140° to 145° for about a half hour. Considerable tar was formed and on crystallizing from benzene it melted constantly at 155°, sintering at about 150°. When it was crystallized from dilute acetic acid or dissolved in alkali and precipitated by carbon dioxide, the stable thiohydantoïn was obtained which melted at 163° to 164°. Whether the product melting at 155° is simply impure stable hydantoïn or not must be decided later.

Paraphenetylthiohydantoic Acid was obtained on concentrating the aqueous alcoholic filtrates from the rhodanide and the labile hydantoïn. It separated as an insoluble powder, which, after boiling with alcohol and benzene, decomposed at about 212° with effervescence. A nitrogen determination gave :

	Calculated for $C_{11}H_{14}O_3N_2S$.	Found.
N	11.02	11.08

This acid readily dissolves in dilute alkali, and carbon dioxide precipitates the material unaltered.

Stable Paraphenetylpseudothiohydantoïn was obtained from the alcohol and benzene extracts mentioned above. It was precipitated as a white powder by petroleum ether, and it melted at 163° to 164°. A nitrogen determination gave :

	Calculated for $C_{11}H_{12}O_2N_2S$.	Found.
N	11.86	11.77

This hydantoïn is very soluble in benzene and alcohol. It can be crystallized from a mixture of benzene and petroleum ether, or from dilute acetic acid. It agreed in every respect with the compound hitherto supposed to be the rhodanide.

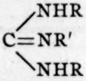
NEW HAVEN, CONN., May, 1902.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

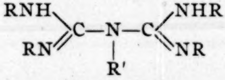
II.—ON THE PREPARATION OF AROMATIC GUANIDINES.

BY FREDERICK J. ALWAY AND CAREY E. VAIL.

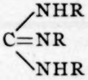
While symmetrical triphenylguanidine is a well-known compound that has been prepared by a great variety of methods, and that can be obtained in pure condition without difficulty, the diphenyltolyl- and phenylditolylguanidines have been but little studied and their properties and reactions are even yet unknown, except in a very small number of cases. The influence of the position of a substituting group upon the course of the reactions in which the guanidines are formed appears to be very great. Marckwald[1] has shown that when an aromatic carbodiimide, $C(=N \cdot R)_2$, reacts with an aniline, $NH_2.R'$, compounds of three different classes may result, *viz.*:



I.



II.



III.

Diphenylcarbodiimide forms with aniline and with *p*-toluidine compounds I. and II., but with *o*-toluidine only a compound of type I. is formed. Di-*o*-tolylcarbodiimide with aniline forms I. and III. As these are the only cases in which the reactions have hitherto been studied, no generalization can safely be made as to the cause of the varying course of the reaction. Of the ten possible isomeric symmetrical tritolylguanidines only two, tri-*o*-tolyl- and tri-*p*-tolylguanidine, are known, and neither of these has been investigated to determine whether diguanides are formed at the same time. Of the six possible symmetrical phenylditolylguanidines only phenyl-di-*o*-tolylguanidine has been prepared. Of the three diphenyltolylguanidines only *p*-tolyl- and *o*-tolyl- compounds have been obtained. Diphenyl-*p*-tolylguanidine was obtained by Hofmann,[1] and later by Huhn,[2] and carefully investigated by Marckwald,[3] who also studied the formation and properties of diphenyl-*o*-tolylguanidine. Diphenyl-*m*-tolylguanidine has been prepared in this laboratory and will be described in a subsequent article. So, of the twenty possible symmetrical guanidines containing only phenyl or tolyl, or phenyl and tolyl groups, but four have hitherto been carefully studied, and in the formation of these four, as above pointed out, we have three different types of reactions.

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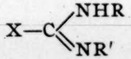
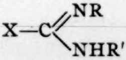
[1] Ann. Chem. (Liebig), **286**, 343.

While the preparation of triphenylguanidine presents no difficulties, that of the diphenyltolylguanidines and the phenylditolylguanidines, using analogous methods, has proved unsatisfactory on account of the difficulty of obtaining the pure base from the reaction-mixture. In 1886 Huhn[4] described two isomeric diphenyl-*p*-tolylguanidines, melting at 120° and 126° respectively. In the last edition of Beilstein these compounds are described as isomers. It was not easy to understand why these compounds should be accepted as isomers without the repetition of Huhn's work, when they, with the exception of a few amidines, were the only examples of isomers to which the different structural formulæ


$$\mathrm{X{-}C}\begin{matrix}\diagup \mathrm{NHR}\\ \diagdown\!\!\diagdown \mathrm{NR'}\end{matrix}$$

and


$$\mathrm{X{-}C}\begin{matrix}\diagup\!\!\diagup \mathrm{NR}\\ \diagdown \mathrm{NHR'}\end{matrix}$$

could be assigned, and at a time when Conrad Laar, who introduced the name and the idea of "tautomerism," could make the statement:[5] "Auf jenen (Tautomerie-) Begriff selbst brauche ich an dieser Stelle nicht wieder zurückzukommen, da er inzwischen zu allgemeiner Aufnahme gelangt ist."

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[1] Ber. d. chem. Ges., **2**, 459.

[2] *Ibid.*, **19**, 2412.

[3] *Loc. cit.*

[4] *Loc. cit.*

[5] Sitzungsberichte d. Niederrhein. Ges. f. Natur-u. Heilkunde, **5**, 6 (1893).

The repetition of Huhn's work and the investigation of other members of this class of bases showed that the alcoholic solution of the base, which results from the action of lead oxide upon a mixture of diphenylthiourea (1 mol.) and a toluidine (1 mol.), yielded an amorphous solid or a thick, oily liquid, from which only 2 to 5 per cent of the theoretical amount of guanidine could be obtained. Marckwald, who in 1895 showed that the compounds described by Huhn as isomers were really identical, and that a second base was mixed with the guanidine in the crude reaction-mixture in each case, has very kindly informed us in a private communication that he obtained a better yield from the carbodiimide and base than from the thiourea and base, and that he had no notes of the yield but believed the former method gave at least 20 per cent of the theoretical. By using the carbodiimide we obtained 40 per cent of the theoretical yield in some cases. Even when we used this method it was often found difficult to obtain the guanidine in pure condition. As the guanidines, when once obtained in pure form, crystallize from alcohol readily, we studied the salts of diphenyl-*p*-tolylguanidine with the idea of finding, if possible, one that could be readily obtained in the pure form and that, with alkalies, would give the pure base. It was found that the nitrate, which is but sparingly soluble in cold alcohol and which crystallizes well from this solvent, could easily be obtained pure, and that the base, liberated from this by an alkali, was practically pure and crystallized readily from alcohol. The same method seems capable of general application in the case of guanidines that contain two phenyl- and one tolyl- or one phenyl- and two tolyl- groups. The simplest method of preparing triphenylguanidine is that of Hofmann.[1] A mixture of aniline (1 mol.) and diphenylthiourea (1 mol.), in concentrated alcoholic solution, is treated with lead oxide or mercuric oxide. Various salts of these metals may be used instead of oxides. The mixture is kept boiling on a water-bath until desulphurization is complete and then filtered hot. The triphenylguanidine separates from the cooling filtrate in large, colorless crystals. The yield is almost quantitative.

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[1] Ber. d. chem. Ges., 2, 458.

Starting with carbon bisulphide, aniline, and a lead salt, the guanidine may be had in pure condition within an hour and a half. By using the methods of Hugershoff[1] or Braun,[2] diphenylthiourea may be obtained in pure condition within half an hour, instead of eight to twelve hours as by the older methods. A comparison of the different methods of preparing the thioureas, together with various modifications, is given in the experimental part of this article.

EXPERIMENTAL.

As the aromatic guanidines, with the exception of triphenylguanidine, have been obtained directly or indirectly only from thioureas, a convenient method of preparing the latter was important. Accordingly, we endeavored to determine which of the methods suggested is the most satisfactory. We found that lead hydroxide is a more satisfactory desulphurizing agent than any that has previously been described.

Preparation of Thioureas.

When a mixture of aniline, carbon bisulphide, and alcohol is heated on the water-bath for from three to fifteen hours, the mixture becomes almost solid from the formation of diphenylthiourea. The reaction takes place more quickly if solid potash is added, but the yield is thereby diminished. Hugershoff[3] showed that the reaction, in the above case, is due to the presence of sulphur dissolved in the carbon bisulphide and that, when sulphur was added before heating, the reaction was complete at the end of an hour. Later, Braun[4] showed that by shaking a mixture of aniline (2 mols.) and carbon bisulphide (1 mol.) with an aqueous solution of hydrogen peroxide (1 mol.) the same thiourea was formed. We found that by using only carbon bisulphide (5 parts), aniline (5 parts), and sulphur (1 part), the reaction was practically complete at the end of fifteen minutes. While by Braun's method evolution of hydrogen sulphide is avoided and the reaction takes place as quickly as when the last described method is used, the crude reaction-product, which contains about 10 per cent of sulphur, must be freed from water before it is treated with carbon bisulphide. In both cases the sulphur may be extracted by carbon bisulphide, the diphenylthiourea remaining in pure crystalline condition. Instead of removing the sulphur in this way the unchanged carbon bisulphide may be driven off by warming the reaction-mixture on the water-bath, and the thiourea then recrystallized from alcohol. The first method of purification was found preferable, requiring much less time and giving a better yield of pure thiourea.

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[1] Ber. d. chem. Ges., **32**, 2245.

[2] *Ibid.*, **33**, 2727.

[3] *Loc. cit.*

[4] *Loc. cit.*

Desulphurizing Agents.

The chief of these whose action has hitherto been described are mercuric oxide and lead oxide. The salts of lead and mercury were not found satisfactory, the product consisting of a mixture of base and salt, and the reaction proceeding slowly. The best reagent seems to be lead hydroxide, freshly prepared by treating lead nitrate solution in the cold with ammonium hydroxide and washing the precipitate with water until the diphenylamine test shows the absence of nitrate. The hydroxide is filtered out under suction and mixed with alcohol to form a thin paste. If the reaction-mixture is allowed to become warm or if the hydroxide is preserved for any considerable length of time, the fine precipitate, at first obtained, becomes coarse and granular. When this coarse form is used a great excess of the lead hydroxide is required to desulphurize the thiourea. The small amount of lead compound required, the rapidity of the reaction, and the ease with which its course may be followed, are the chief arguments in favor of its use. On the other hand, it must be freshly prepared and thoroughly washed. If the last precaution is omitted, the hydroxide will contain some ammonium nitrate, which causes the formation of more or less guanidine nitrate.

Preparation of Guanidines.

The thiourea and amine, in equimolecular amounts, are dissolved in ordinary alcohol and the mixture heated to boiling on the water-bath. Then an excess of lead hydroxide, prepared as above described, is added to the mixture and the heating continued until a portion of the filtered alcoholic solution, when boiled with lead hydroxide, produces no blackening. The rate of desulphurization depends upon the nature of the thiourea. Witt has shown that it is probable that the carbodiimide is first formed and that this then combines with the base.

When diphenylthiourea was used the reaction was complete at the end of ten minutes, but when phenyl-*p*-tolylthiourea and di-*p*-tolylthiourea were employed, half an hour and two hours, respectively, were required. The hot reaction-mixture is filtered under suction and the black residue, consisting chiefly of lead sulphide, is extracted with small quantities of boiling alcohol until the last portion, when filtered and treated with an excess of water, remains clear. In the preparation of diphenyl-*p*-tolylguanidine the eighth and ninth portions of alcohol gave a white deposit on cooling. This, when recrystallized, gave colorless needles melting at 128° to 129°, the melting-point of the guanidine. The diguanide, which forms in small quantities and which, being only slightly soluble in aqueous alcohol, remains mixed with the lead sulphide, is evidently decomposed by prolonged heating in alcoholic solution to form the corresponding guanidine. The clear solution contains a large amount of the guanidines, but, on standing, deposits either no crystals at all or at most only from 2 to 5 per cent of the theoretical amount. By complete evaporation of the alcohol a gummy mass is obtained. When the above solution, kept cool by ice-water, is treated with a slight excess of concentrated nitric acid, it becomes red and crystals soon begin to separate out. At the end of two hours the separation is usually complete. The crystals are filtered out, washed with a little cold alcohol, and dried. Sometimes they are colored pink, in which case they are dissolved in alcohol and the solution boiled with animal charcoal. The nitrate so obtained is recrystallized until the melting-point remains constant and then dissolved in warm alcohol. After adding a few drops of phenolphthalein the solution is treated with dilute potash until it shows a faint alkaline reaction. In the preparation of phenyldi-*o*-tolylguanidine a small amount of tri-*o*-tolylguanidine is formed at the same time. It was found that to obtain the latter compound it was best to change the mixture of nitrates, after it had been once recrystallized from alcohol, into the corresponding guanidines which were then separated by recrystallization.

In the preparation of diphenyl-*p*-tolylguanidine, the formation of no other guanidine was detected. When the nitrate in this case was recrystallized from alcohol until the melting-point remained constant, the pure base could be obtained by treating the warm solution of the nitrate in aqueous alcohol with dilute potash, and then allowing it to cool slowly.

In all cases investigated, with the exception of tri-*m*-tolylguanidine, the yield of nitrate or of the mixture of nitrates was from 75 to 90 per cent of the theoretical. The nitrate of tri-*m*-tolylguanidine was not obtained by the general method.

As the whole subject of the action of aromatic amines upon carbodiimides as well as upon thioureas is under investigation in this laboratory, we will describe only the nitrate of diphenyl-*p*-tolylguanidine of which the corresponding base and hydrochloride have been previously described by Marckwald.[1]

Diphenyl-*p*-tolylguanidine nitrate was obtained in equally good yield from diphenylthiourea with *p*-toluidine, and from phenyl-*p*-tolylthiourea with aniline. It forms small, colorless plates, melting at 196° to 197°, readily soluble in hot alcohol, slightly soluble in cold alcohol and hot water, and very slightly soluble in cold water.

	Calculated for $C_{20}H_{19}N_3.HNO_3$.	Found.
HNO_3	17.30	17.68

The nitrates of the following bases have been obtained by the general method given above: diphenyl-*m*-tolyl-, phenyldi-*p*-tolyl-, *o*-tolyldi-*p*-tolyl-, *m*-tolyldi-*p*-tolyl-, di-*o*-tolyl-*p*-tolyl-, di-*o*-tolyl-*m*-tolyl-, and phenyl-*o*-tolyl-*p*-tolylguanidine.

UNIVERSITY PLACE, May, 1902.

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[1] *Loc. cit.*